Oak Ridge National Laboratory

Low-Temperature Emission Control to Enable Fuel-Efficient Engine Commercialization

Todd J. Toops (PI)
Email: toopstj@ornl.gov
Phone: 865-341-1207

Oak Ridge National Laboratory
National Transportation Research Center

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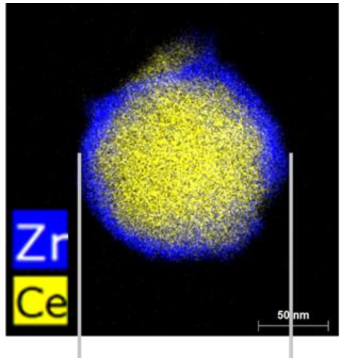
Acknowledgments

- **Funding & guidance from DOE VTO Program Managers:**
  - Siddiq Khan, Ken Howden, Gurpreet Singh, Mike Weismiller

- **Contributions from the ORNL Team:**
  - Pranaw Kunal, Michelle Kidder, and Michael Lance

- **Collaboration with University At Buffalo:**
  - Judy Liu, Junjie Chen, Prof. Eleni Kyriakidou



- **Access to instrumentation at ORNL:**
  - Micrographs and elemental maps captured using instrumentation (FEI Talos F200X S/TEM) provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program and the Nuclear Science User Facilities

Project Overview

Timeline

- Year 2 of 3-year program
  - **Project start date:** FY2019
  - **Project end date:** FY2021
- Builds on previous R&D in FY16-FY18

Budget

- FY20: $500k (Task 1*)

*Task 1: Low Temperature Emissions Control Catalysis Research

Part of large ORNL project "Controlling Emissions from High Efficiency Combustion Systems" (2018 VTO AOP Lab Call)

Barriers Addressed

U.S. DRIVE Advanced Combustion & Emission Control 2018 Roadmap Barriers & Targets:

- Addressing emission compliance barrier to market for advanced fuel-efficient engine technologies, such as 90% conversion of NOx, CO and HC at 150°C
- Efficiency, durability, sulfur tolerance of aftertreatment systems

Collaborators & Partners

- US DRIVE Advanced Combustion and Emission Control Tech Team
- University at Buffalo (SUNY)
- Harvard University/Metalmark Innovations
- Chalmers University

Challenging emissions/efficiency regulations dictate need for new technology

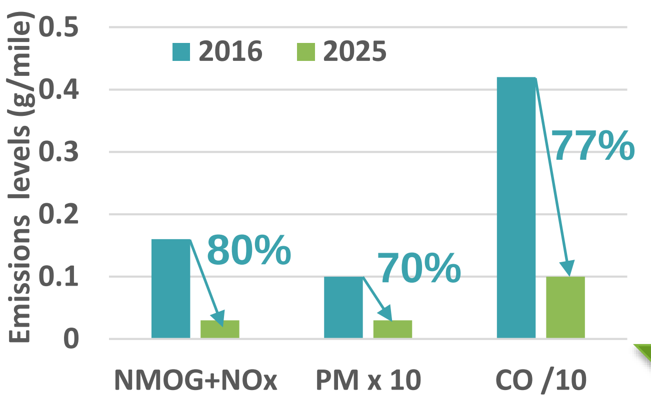
Develop new emission control technologies to enable fuel-efficient engines with low exhaust temperatures (<150°C) to meet emission regulations. Goal: 90% Conversion at 150°C

- Greater efficiency lowers exhaust temperature
- Catalysis is challenging at low temperatures
- Emissions standards getting more stringent
  - Moving towards zero

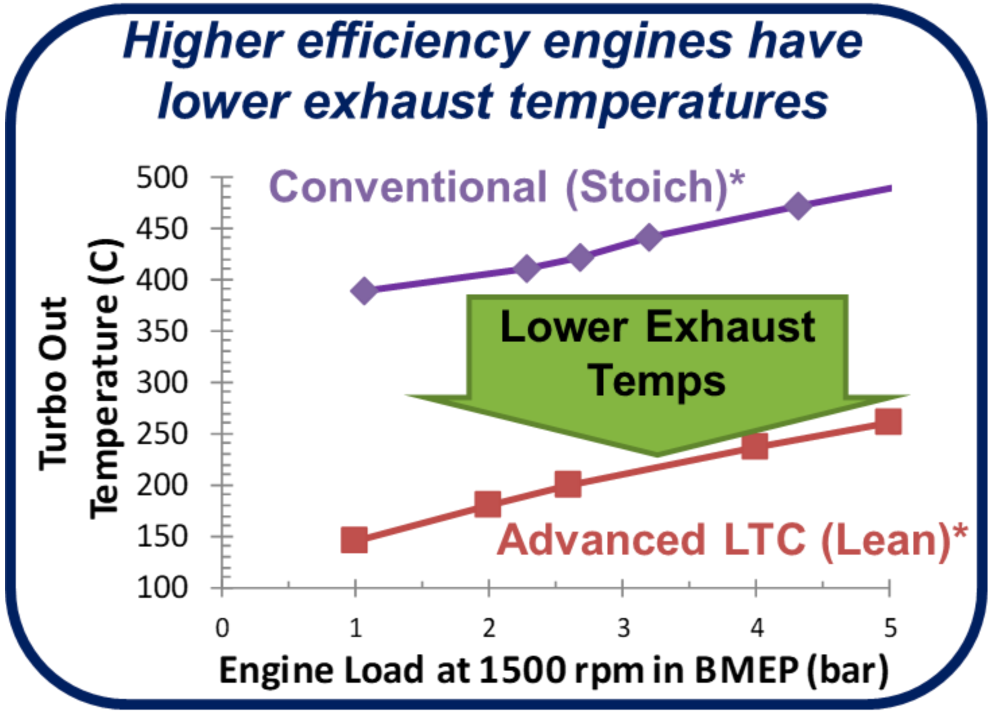
Fuel Economy

Fuel Economy Drivers

- *CAFE standards*
- *CO_2 emissions standards*
- *Consumer demand/cost of ownership*



Emissions



* "**Conventional**": modern state-of-the-art GDI Turbocharged (stoichiometric)
* "**Advanced LTC**": advanced lean-burn Low Temperature Combustion (LTC) engine

Guiding Documents Define Industry Needs

2017 CLEERS Industry Priorities Survey

USDRIVE "The 150ºC Challenge" Workshop Report

USDRIVE ACEC Tech Team Roadmap (2018)

Relevant to all combustion approaches cited in ACEC Tech Team Roadmap

Identified Needs Addressed:

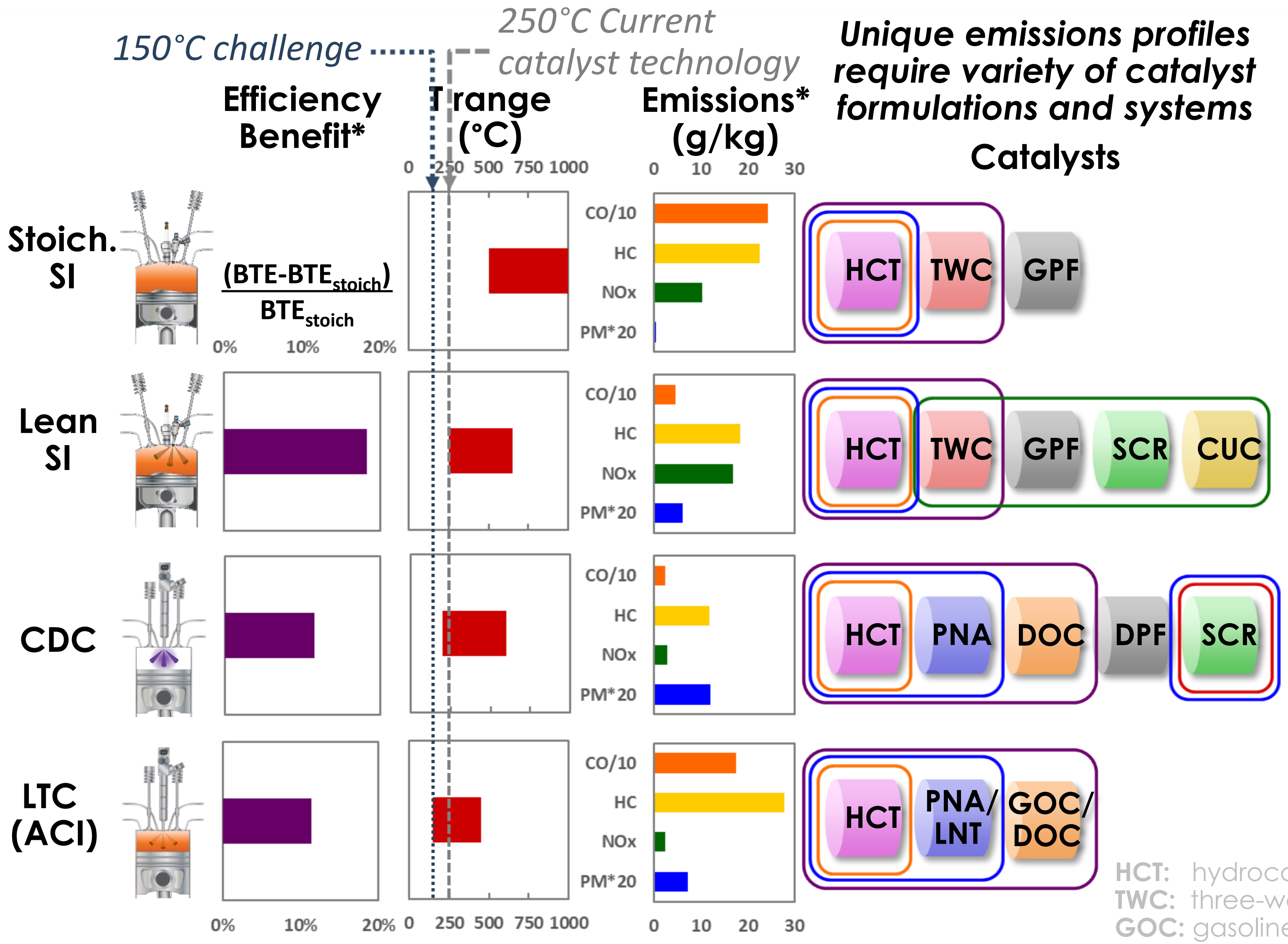
- **Lower temperature CO and HC oxidation**
- **Low temperature NOx reduction**
- **Cold start emission trapping technologies**
  - Especially passive NOx adsorbers
- **Reduced PGM**
- **Better durability**
- **Promote innovative catalytic solutions via partnering with DOE BES programs**

Low Temperature Combustion (LTC)

Dilute Gasoline Combustion

Clean Diesel Combustion (CDC)

Low temperature emissions control challenges affect multiple platforms



*(efficiency and emissions at 2000 rpm, ~2 bar BMEP)

ORNL R&D portfolio spans wide range of applications, technologies, size scales, commercial readiness

Projects

CLEERS (ACE022)
Model new trap materials and aging effects on SCR catalysts

Low Temperature Emissions Control (ACE085)
Discover new low T catalysts & traps

Lean Gasoline Emissions Control (ACE033)
Develop pathways for lean gasoline engines to meet emissions with minimum fuel penalty

Chemistry & Control of Cold Start Emissions (ACE153)
Understand how exhaust chemistry impacts device performance & design

Cummins Emissions Control CRADA (ACE032)
Understand how aging affects properties and performance of SCR catalysts

HCT: hydrocarbon trap
TWC: three-way catalyst
GOC: gasoline oxidation catalyst
DOC: diesel oxidation catalyst
LNT: lean NOx trap
SCR: selective catalytic reduction
CUC: CO/HC clean-up catalyst
GPF: gasoline particulate filter
DPF: diesel particulate filter
PNA: passive NOx adsorber

Employing US DRIVE protocols to evaluate novel catalysts

- Project employs US DRIVE Advanced Combustion and Emission Control Team Aftertreatment Protocols for Catalyst Characterization and Performance Evaluation
- Full suite of protocols at: www.CLEERS.org and in literature[†]

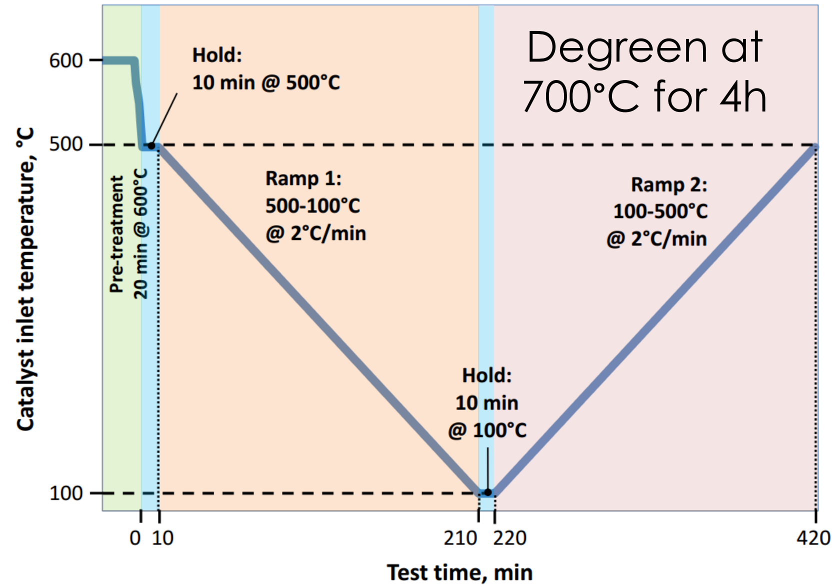
LTC-D: Low Temp. Combustion Diesel	
Total HC_1:	3000 ppm
C_2H_4:	500 ppm
C_3H_6:	300 ppm
C_3H_8:	100 ppm
***$C_{12}H_{26}$:**	**2100 ppm**
CO:	2000 ppm
NO:	100 ppm
H_2:	400 ppm
H_2O:	6 %
CO_2:	6 %
O_2:	12 %
Balance N_2	

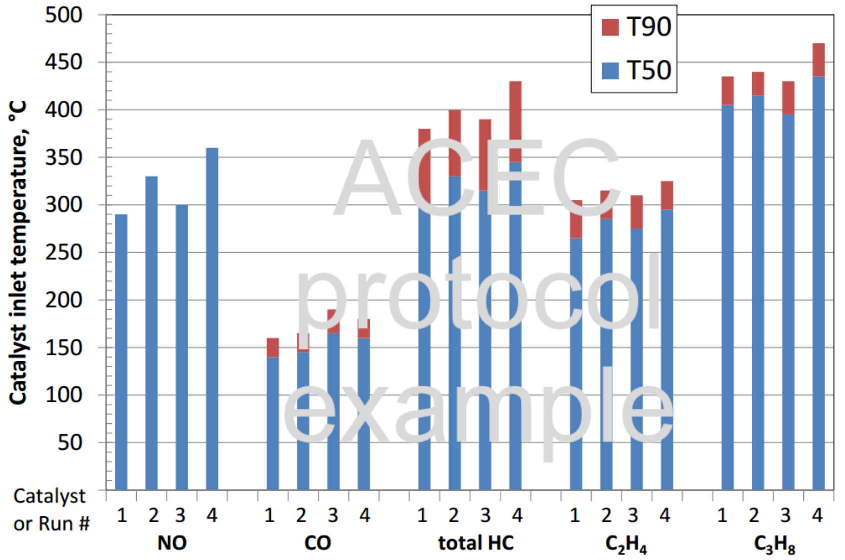
* - we employed decane ($C_{10}H_{22}$) due to bubbler needs

S-GDI: Stoich. Gasoline Direct Injection	
Total HC_1:	3000 ppm
C_2H_4:	1050 ppm
C_3H_6:	1500 ppm
C_3H_8:	450 ppm
i-C_8H_{18}:	0 ppm
CO:	5000 ppm
NO:	1000 ppm
H_2:	1670 ppm
H_2O:	13 %
CO_2:	13 %
O_2:	0.74 %
Balance N_2	

Powder Catalyst Requirements

- Reactor ID 3-13 mm
- Catalyst particle size ≤ 0.25 mm
- Catalyst bed L/D≥1
- Space velocity
  - 200-400 L/g-hr
  - For 0.1 g, flow 333-666 sccm





† - K.G. Rappé et al. Emission Control Science and Technology 5:2 (2019) 183-214.

Wide-ranging collaborations to maximize progress and relevance

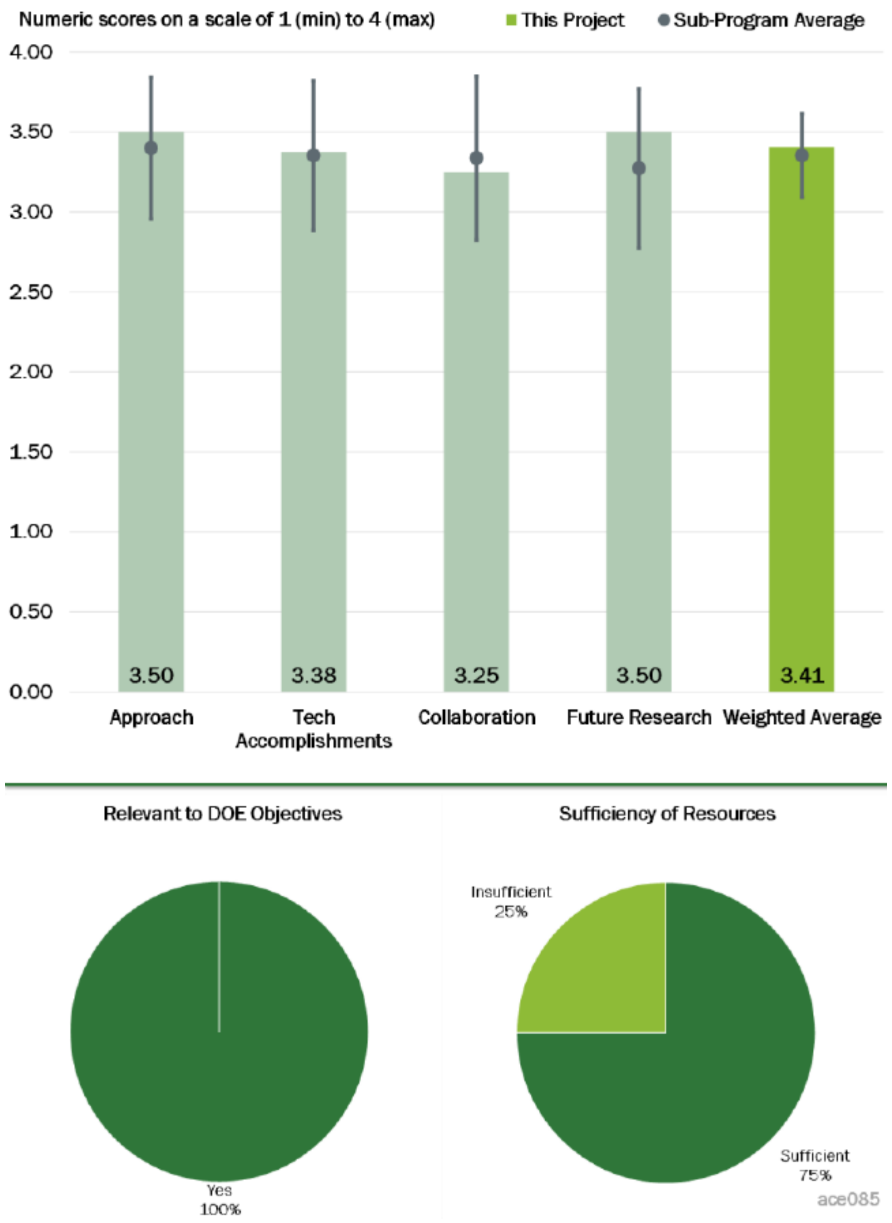
- **Academia**
  - **University at Buffalo (SUNY):** Catalyst synthesis/characterization/eval.; Prof. Eleni Kyriakidou, Judy Liu, Junjie Chen
  - **Harvard University:** Wyss Institute for Biologically Inspired Engineering, Prof. Joanna Aizenberg
    - Synthesis of new structured and stable catalysts (PGM supported on metal oxides); evaluated at ORNL
  - **Chalmers University of Technology:** Synthesis of LTA zeolites for PNA, Prof. Louise Olsson and Aiyong Wang
  - **Karlsruhe Institute of Technology:** joint paper on oxidation catalysts with Olaf Deutschmann
- **Industry**
  - **USCAR/USDRIVE Low Temperature Aftertreatment (LTAT) working group**
    - low temperature evaluation protocols, discussions about industry research needs
  - **Metalmark Innovations:** Spinoff company associated w/technology from Harvard University; Tanya Shirman & Sissi Liu
  - **Johnson Matthey:** Industry input from Haiying Chen; partner on DOE project Sharan Sethuraman
- **DOE Basic Energy Science researchers**
  - Sheng Dai and Ashi Savara (ORNL), Center for Nanophase Materials Science
    - Catalysts synthesis, characterization, and modeling synergistic relationships
- **Other DOE funded projects**
  - **CLEERS:** Dissemination of data; presentation at CLEERS workshops
  - **PNNL:** periodic teleconferences established to share data on VTO projects; shared evaluation of technologies
  - **University of Houston-led project with University of Virginia, Johnson Matthey, Southwest Research Institute**

Milestones of 3-year project

- FY19 Milestones: ***met***
  - Determine ion-exchange/nanoparticle distribution in HCT/PNA
- FY20 Milestones: ***on track***
  - Determine which multifunctional configuration yields the highest activity while simulating cold start heating rates using the top performing HC Trap/PNA + DOC
- FY21 Milestones: ***on track***
  - Demonstrate 90% conversion of criteria pollutants CO, HC, and NOx at 150°C on hydrothermally-aged catalysts

Response to reviewer comments

- **REVIEWER:** Emphasis should be on the gradual deterioration of NOx storage efficiency on repeated cold-start tests. Solutions to this deterioration need to be explored, either through catalyst changes or system modifications
  - *This was the primary focus of PNA research this year; identified primary deactivation agent*
- **REVIEWER:** For PNA and HC trap…suggested that a re-evaluation of this work should take that into consideration for either improving this technology or moving to a new material
  - *New materials have been synthesized that include bi-metallic ion-exchanged SSZ-13 and a new zeolite (LTA)*
- **REVIEWER:** the aging protocol currently being used, 800°C seems overly aggressive for these materials, as compared to what temperatures they may see in use…[look into] effect of a temperature sweep (between 700°C-850°C, every 25°C) on the material
  - *Included several example of lesser-aged materials in presentation this year*

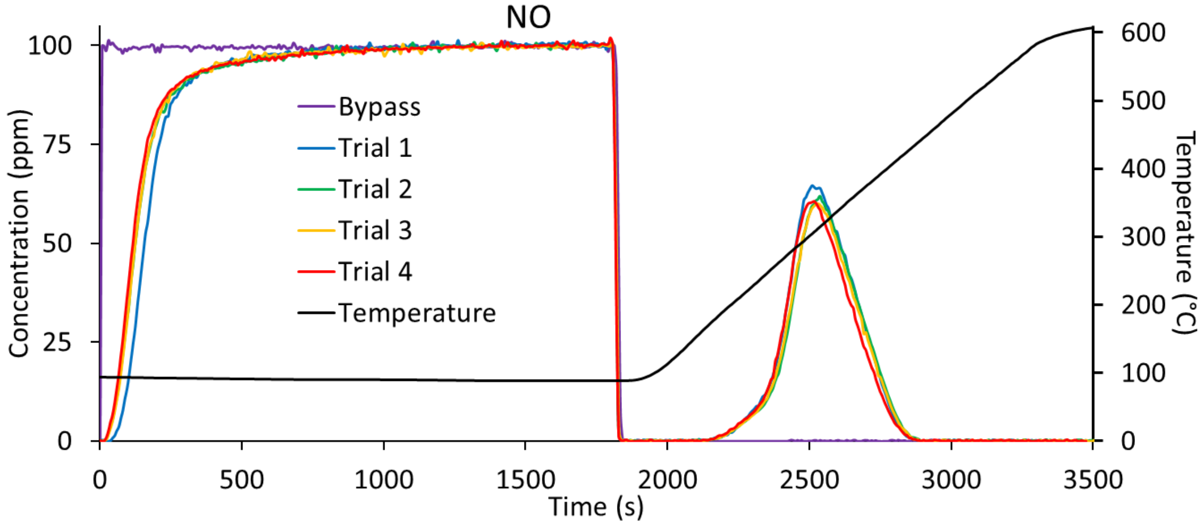


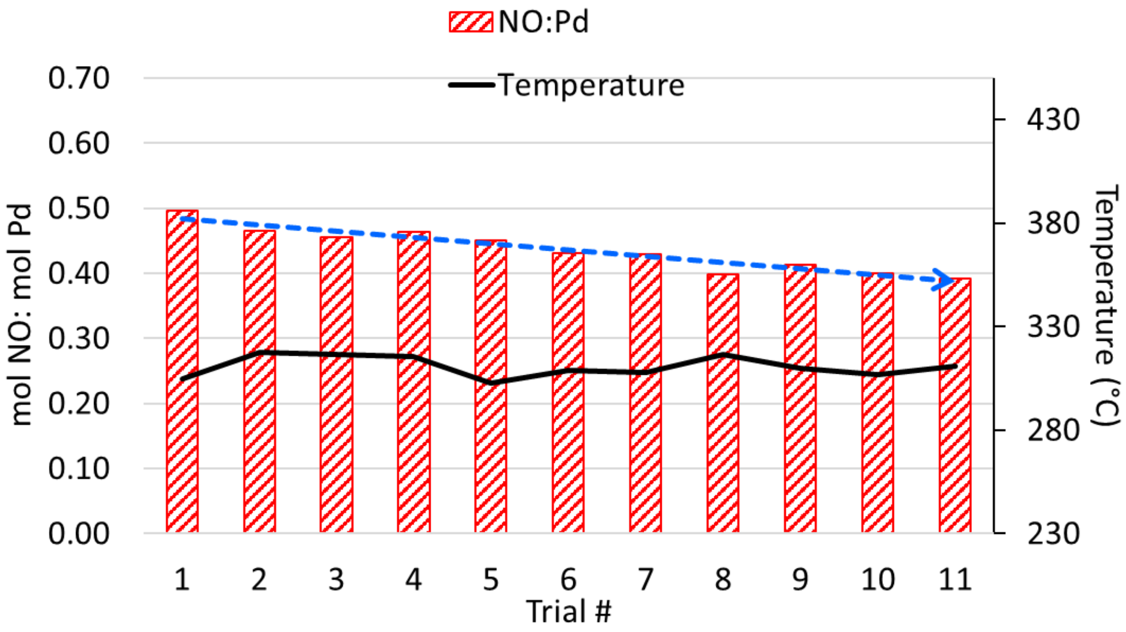
Technical Accomplishments

- Passive NOx Adsorbers
  - Understanding deactivation
  - Investigating new formulations
- Oxidation Catalysts
  - Core-shell PGM support
  - Metalmark Innovation porous PGM support
- Stoichiometric TWCs
  - Applying novel catalysts as TWCs

Passive NOx Adsorbers (PNAs) show a gradual degradation in NOx uptake with repeated evaluations using fully simulated exhaust flows

- PNA for this evaluation is 1% Pd/SSZ-13
  - Commercial zeolite purchased
  - Pd addition performed at ORNL
- Up to 10 trials needed to fully observe deactivation
- Understanding this process and investigating mitigation strategies has been focus of research this year





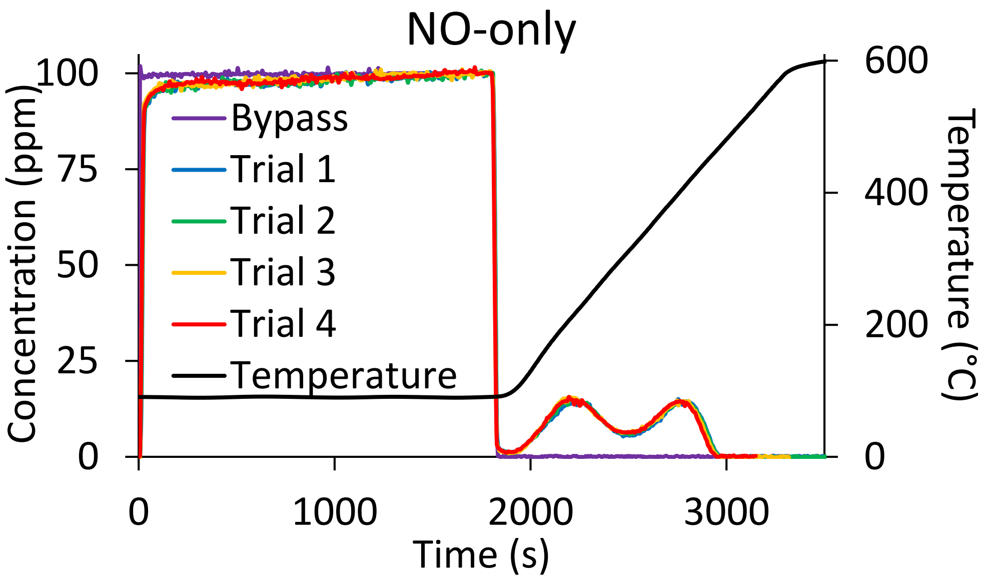
PNA
1% Pd/SSZ-13
Degreened
700 °C, 4 h

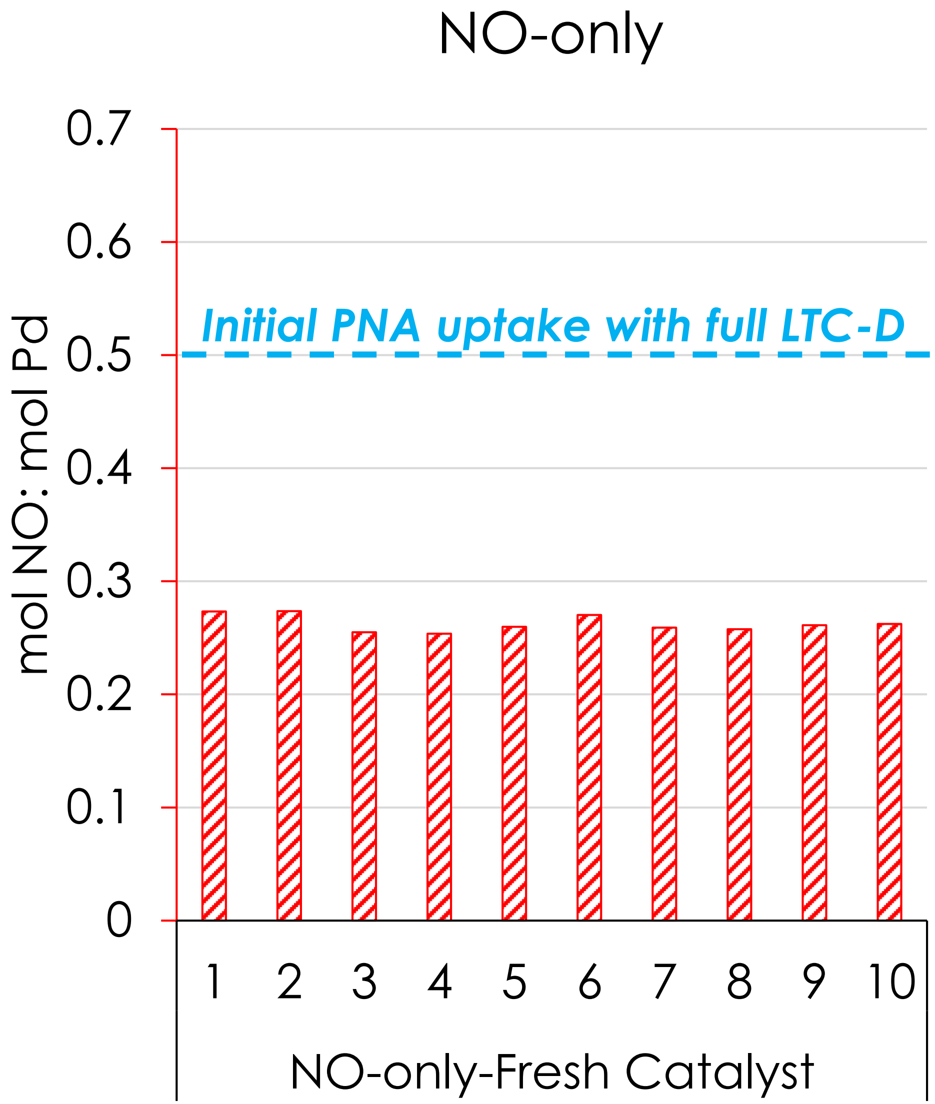
LTC-D: Low Temp. Combustion Diesel

Total HC_1:	3000 ppm
C_2H_4:	500 ppm
C_3H_6:	300 ppm
C_3H_8:	100 ppm
$C_{10}H_{22}$:	2100 ppm
CO:	2000 ppm
NO:	100 ppm
H_2O:	6 %
CO_2:	6 %
O_2:	12 %
Balance Ar	

Repeated evaluations with only NO show lower overall uptake, but not significant degradation

- Release profile is notably different than when flowing the full LTC-D
- Overall NOx uptake decreases by about 50% of the initial LTC-D value
- Removing reductants has large impact on functionality





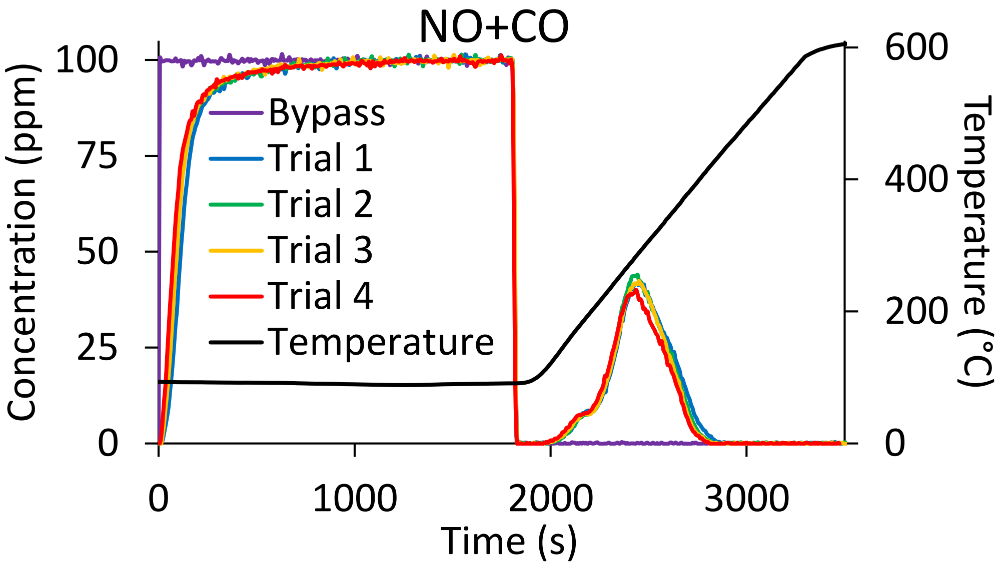
PNA
1% Pd/SSZ-13
Degreened
700 °C, 4 h

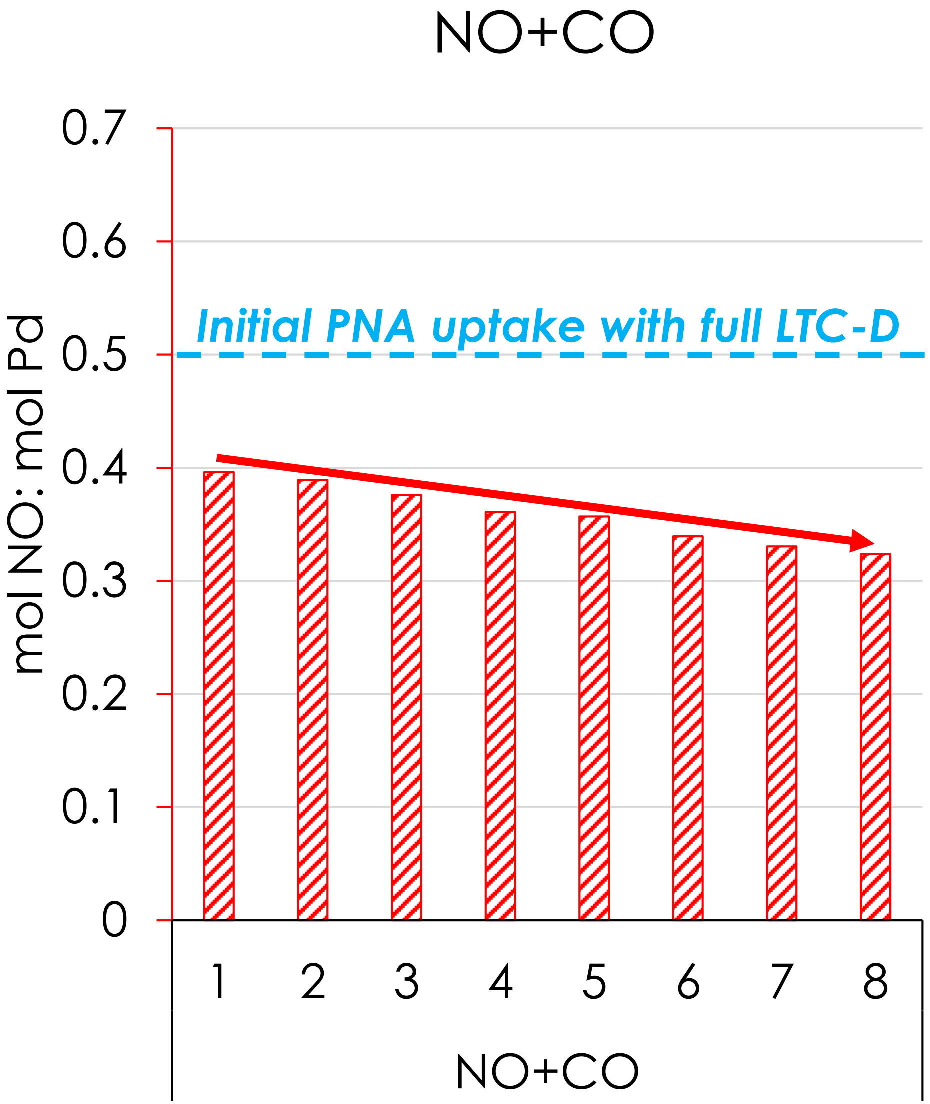
NO-only

Total HC_1:	0 ppm
C_2H_4:	0 ppm
C_3H_6:	0 ppm
C_3H_8:	0 ppm
$C_{10}H_{22}$:	0 ppm
CO:	0 ppm
H_2:	0 ppm
NO:	**100 ppm**
H_2O:	6 %
CO_2:	6 %
O_2:	12 %
Balance Ar	

Adding CO initiates degradation as NOx uptake/release gradually decreases

- Release profile more closely resembles full LTC-D
- Overall NOx uptake higher than NO-only, but starts decreasing significantly
- Addition of CO clearly leads to deactivation…do all reductants cause this?





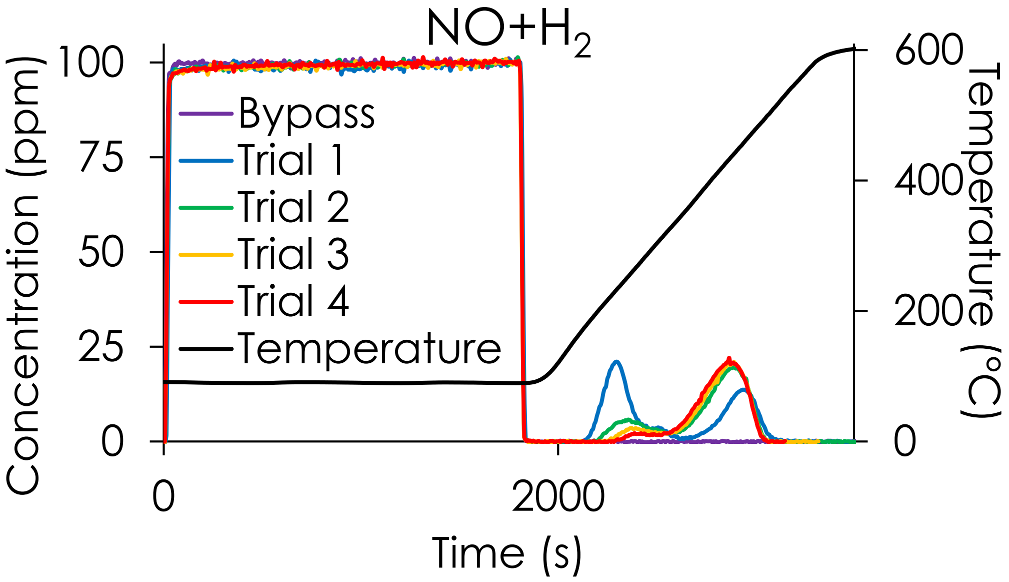
PNA
1% Pd/SSZ-13
Degreened
700 °C, 4 h

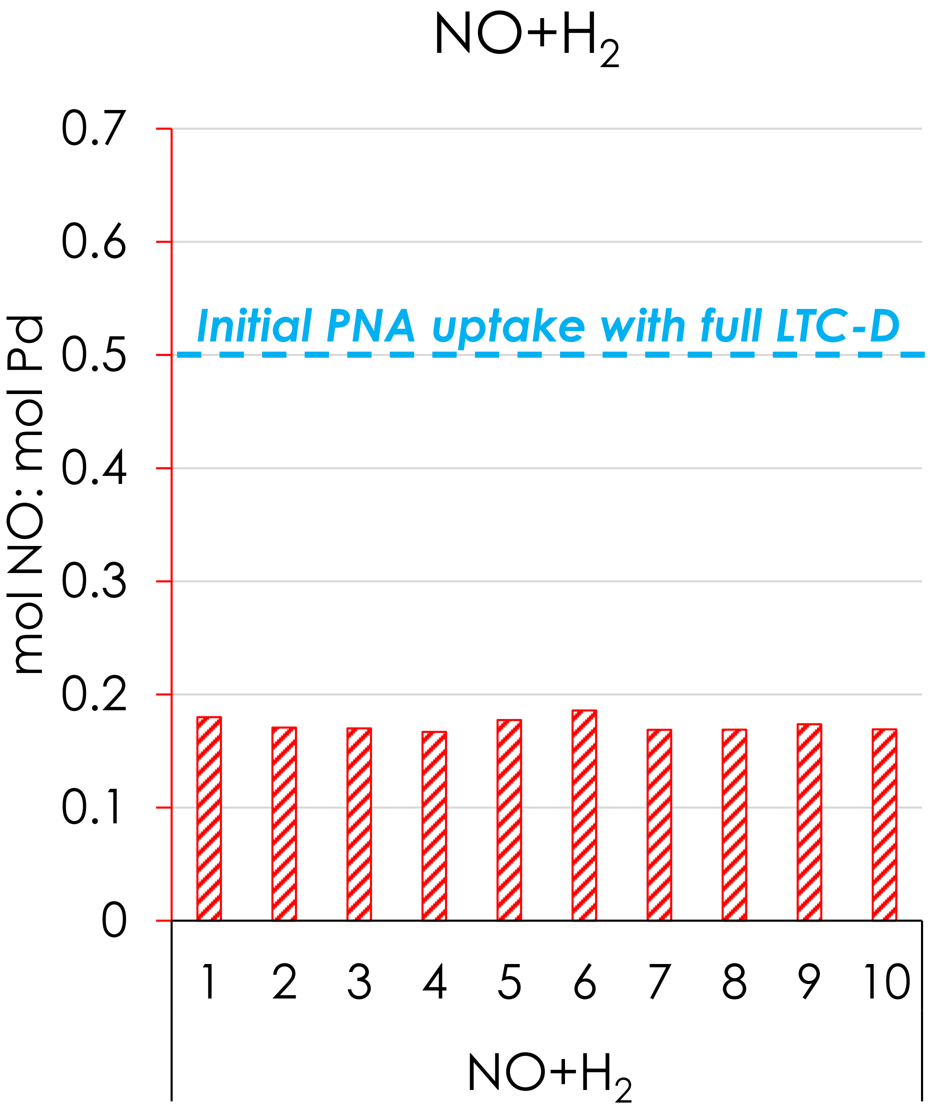
NO+CO

Total HC_1:	0 ppm
C_2H_4:	0 ppm
C_3H_6:	0 ppm
C_3H_8:	0 ppm
$C_{10}H_{22}$:	0 ppm
CO:	**2000 ppm**
H_2:	0 ppm
NO:	**100 ppm**
H_2O:	6 %
CO_2:	6 %
O_2:	12 %
Balance Ar	

H_2 does not lead to deactivation nor does it enhance NOx uptake

- Release profile initially looks like NO-only, but shifts to more closely resemble full LTC-D after 4 trials
- Overall NOx uptake even lower than NO-only, but is stable
- H_2 does not deactivate like CO, but also does not enhance uptake





PNA
1% Pd/SSZ-13
Degreened
700 °C, 4 h

NO+H_2

Total HC_1:	0 ppm
C_2H_4:	0 ppm
C_3H_6:	0 ppm
C_3H_8:	0 ppm
$C_{10}H_{22}$:	0 ppm
CO:	0 ppm
H_2:	**1000 ppm**
NO:	**100 ppm**
H_2O:	6 %
CO_2:	6 %
O_2:	12 %
Balance Ar	

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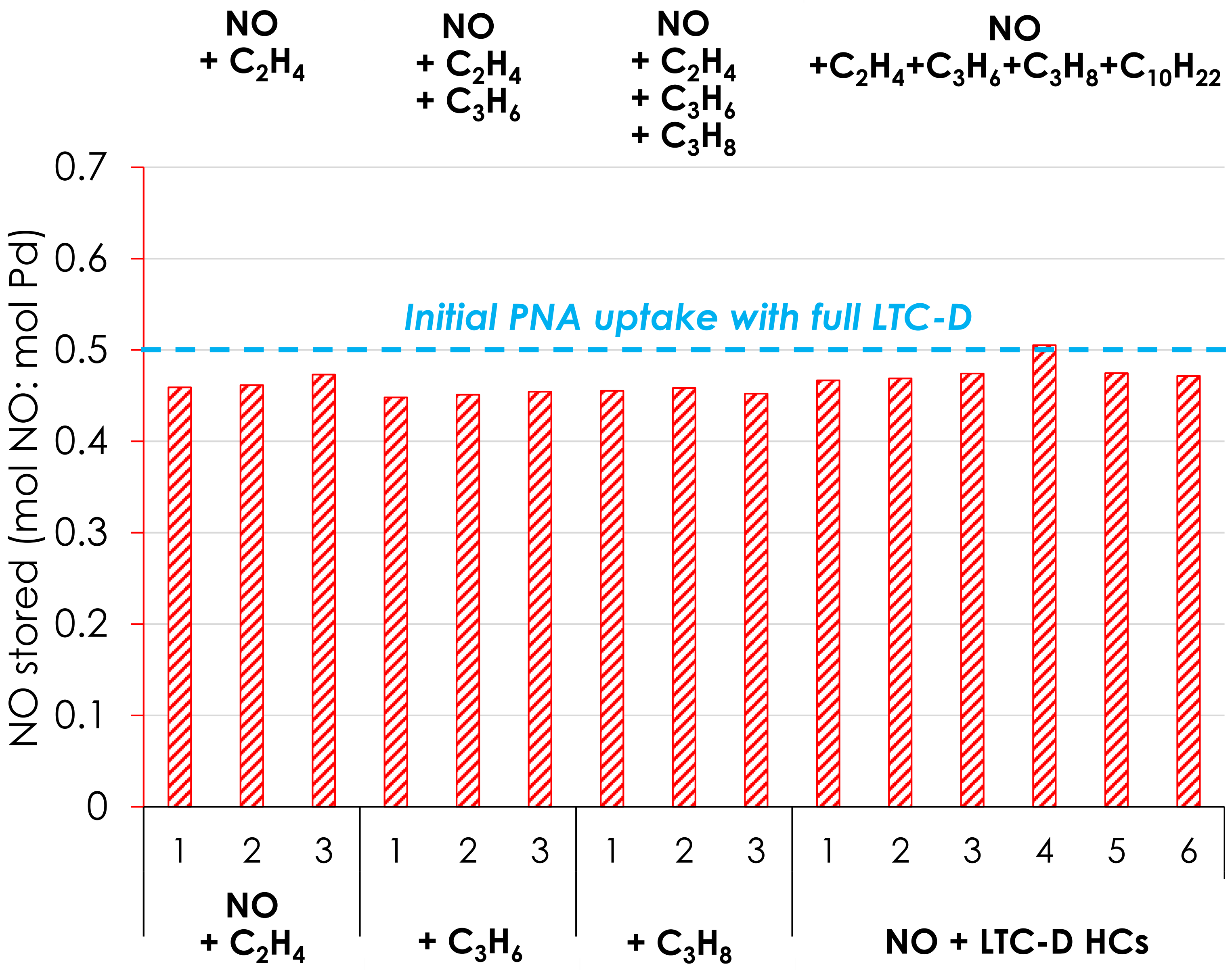
NOx+HCs indicate enhanced NOx storage with no indication of deactivation

- HCs added sequentially in the following sequence
- Regardless of the HC included there is no indication of deactivation
- Do all HCs lead to enhanced NOx uptake?



PNA
1% Pd/SSZ-13
Degreened
700 °C, 4 h

NO+HCs

Total HC_1:	**3000 ppm**
C_2H_4:	500 ppm
C_3H_6:	300 ppm
C_3H_8:	100 ppm
$C_{10}H_{22}$:	2100 ppm
CO:	0 ppm
H_2:	0 ppm
NO:	**100 ppm**
H_2O:	6 %
CO_2:	6 %
O_2:	12 %
Balance Ar	

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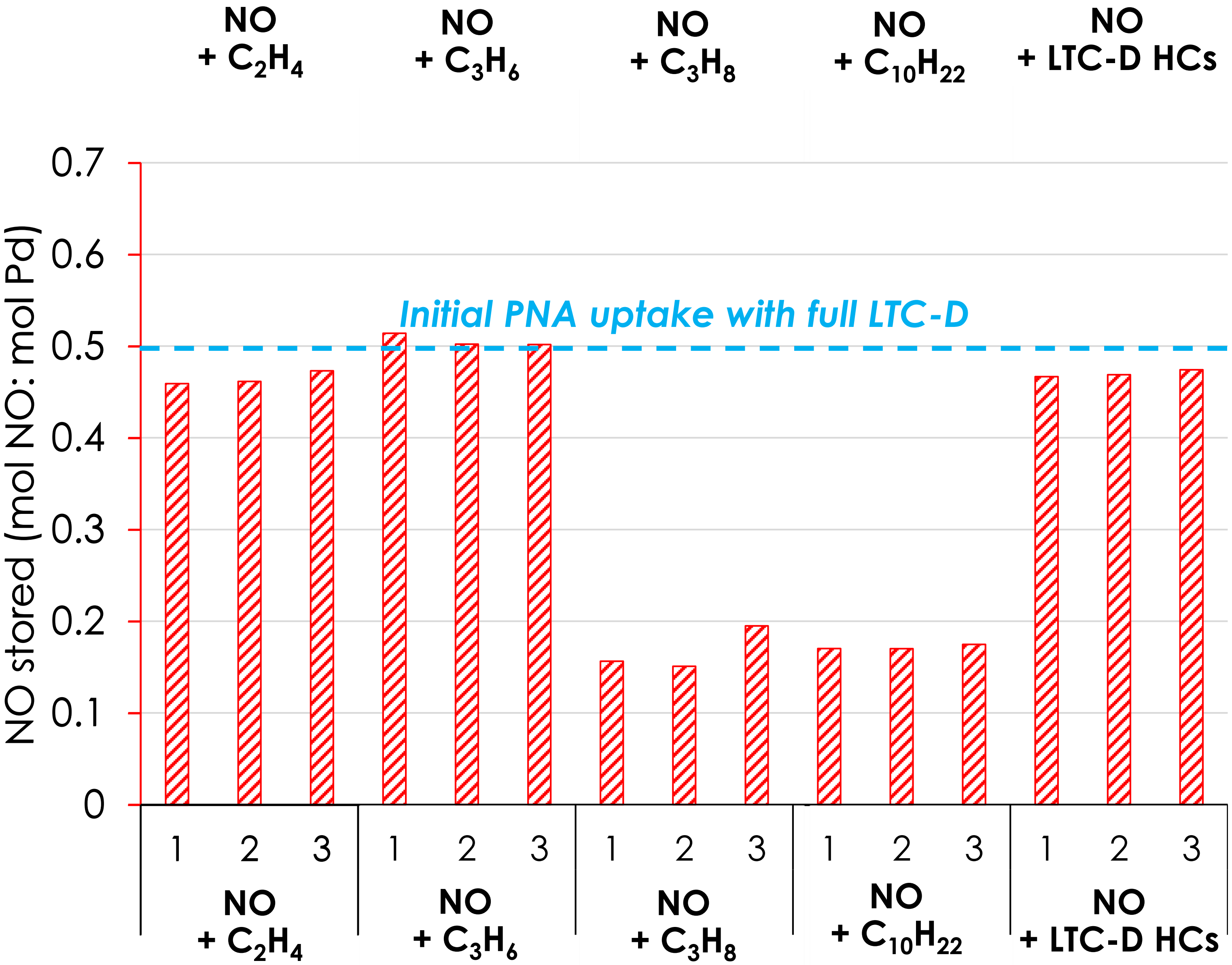
Ethylene and propene show enhanced NOx uptake; not propane/decane

- Evaluated NO uptake in the presence of individual HCs
- Unsaturated HCs that can access the zeolite pores enhance NOx uptake
  - Saturated HCs do not
- Uptake is stable across all HCs evaluated



PNA
1% Pd/SSZ-13
Degreened
700 °C, 4 h

NO+HCs

Total HC_1:	**3000 ppm**
C_2H_4:	500 ppm
C_3H_6:	300 ppm
C_3H_8:	100 ppm
$C_{10}H_{22}$:	2100 ppm
CO:	0 ppm
H_2:	0 ppm
NO:	**100 ppm**
H_2O:	6 %
CO_2:	6 %
O_2:	12 %
Balance Ar	

Additional PNA materials being synthesized and evaluated using bimetallic systems and LTA-zeolites

- Primary goal is to identify more stable PNA material
- Additional goal is Pd reduction in PNA
- Total metal loading is normalized to 1%wt
- Different support material and synthetic techniques are being used for better stability

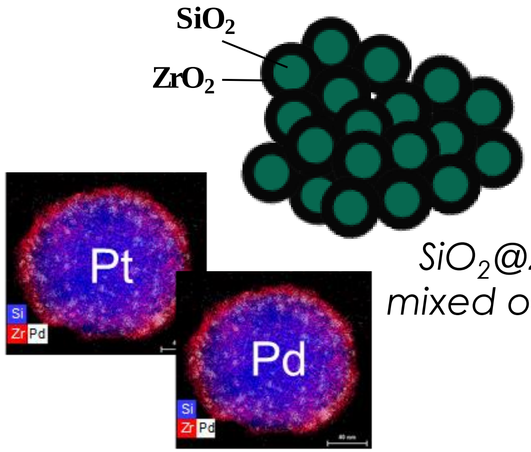
Support Material	Metals	Weight%		Molar Ratio	Method
		Pd	X		
SSZ-13	Pd, Fe	0.66	0.34	1:1	Ion-exchange
SSZ-13	Pd, Co	0.64	0.36	1:1	Ion-exchange
SSZ-13	Pd, Ag	0.50	0.50	1:1	Ion-exchange
SSZ-13	Pd, Cu	0.63	0.37	1:1	Ion-exchange
LTA	Pd	1.00	n.a.	n/a	Ion-exchange
LTA	Pd, Cu	0.63	0.37	1:1	Ion-exchange

Technical Accomplishments

- Passive NOx Adsorbers
  - Understanding deactivation
  - Investigating new formulations
- Oxidation Catalysts
  - Core-shell PGM support
  - Metalmark Innovation porous PGM support
- Stoichiometric TWCs
  - Applying novel catalysts as TWCs

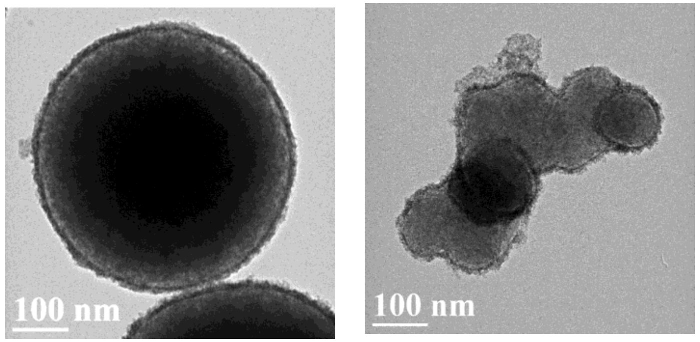
Employing unique high surface area supports for Pt and Pd to achieve 150 °C goal and investigating pathways to limit PGM content

- Supports continue to show good initial THC reactivity, but not reaching 90% conversion until ~250 °C after hydrothermal aging*
- Additional Pd, Pt, and Pt+Pd oxidation catalysts have been synthesized over the past year
  - Other core shell materials with varying diameter: SiO_2@CeO_2, SiO_2@CeO_2-ZrO_2, and CeO_2@ZrO_2
  - Ceria supports including core-only



SiO_2@ZrO_2 mixed oxide

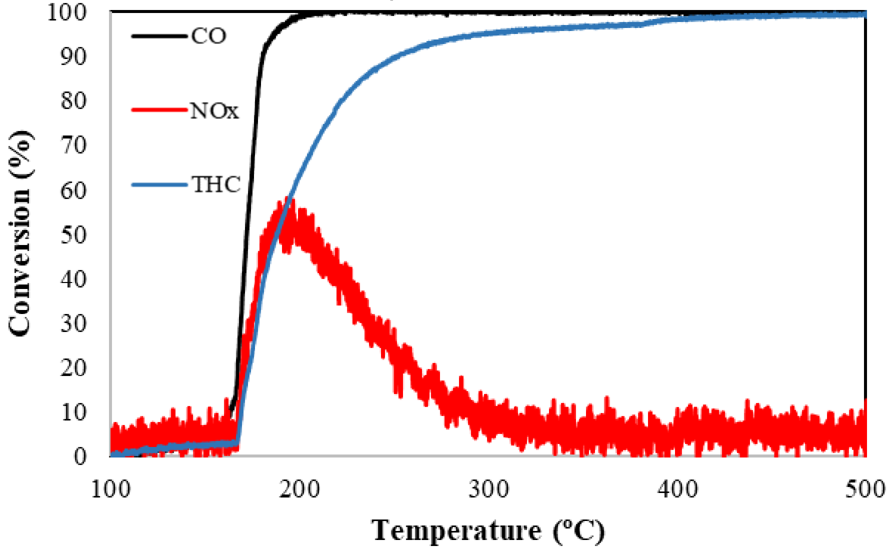
Varying diameter of SiO_2@ZrO_2 initiated with goal of creating surface that is less prone to Pt /Pd sintering

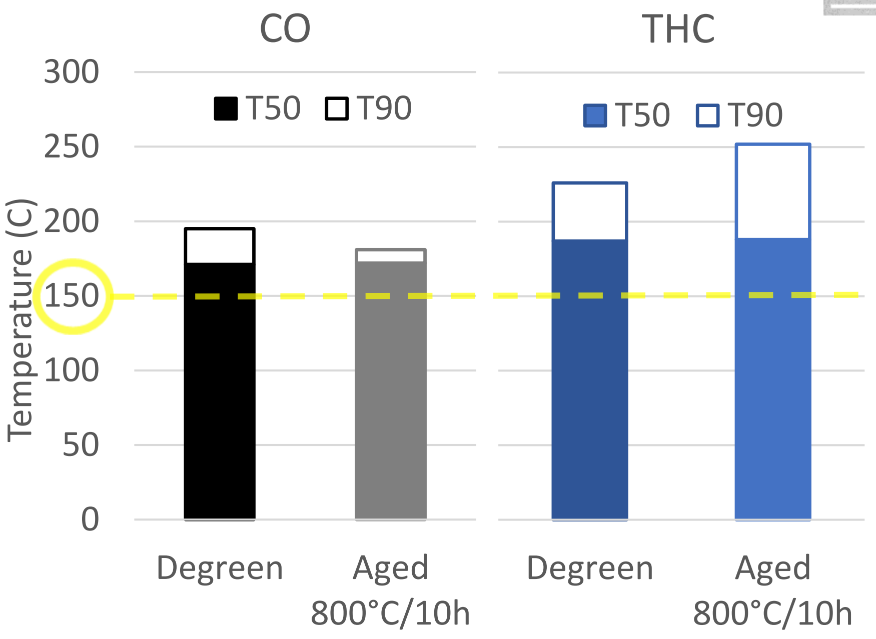


~490 nm <100 nm

Hydrothermally aged at 800 °C for 10h

1% Pd/SiO_2@ZrO_2 + 1.8% Pt/SiO_2@ZrO_2 Physical Mixture





Conditions during 2ºC ramp

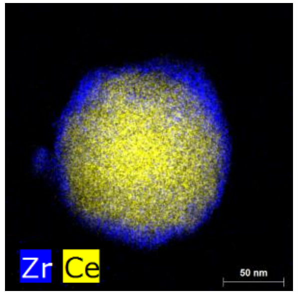
total HC_1:	*3000 ppm*
C_2H_4:	*500 ppm*
C_3H_6:	*300 ppm*
C_3H_8:	*100 ppm*
$C_{10}H_{22}$:	*2100 ppm*
CO:	*2000 ppm*
NO:	*100 ppm*

Also H_2, O_2, H_2O and CO_2

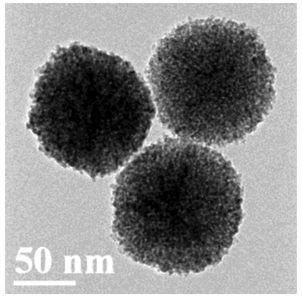
* - E. Kyriakidou, T.J. Toops et al., US patent number 10,427,137 (2019).

Many new oxidation catalyst/support variations evaluated

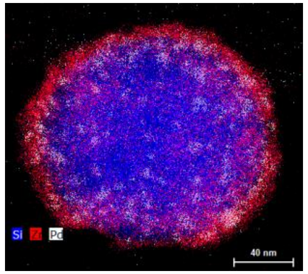
- New synthesis approach with some supports
  - 90 m^2/g ceria obtained with PVP (**P**oly**V**inyl**P**yrrolidone) addition during synthesis
- PGM loading normalized to molar equivalent of 1% Pd
  - varied between 1-1.8% by weight depending on Pt:Pd ratio
  - 1% Pd is the molar equivalent of 1.8% Pt
  - All Pt additions can be viewed as Pd replacement
- Many of these samples show improvement over the initial $Pd/SiO_2@ZrO_2$
  - Bi-metallic $Pd:Pt/SiO_2@ZrO_2$ series showing best initial results
  - Down-selected for additional evaluations and aging



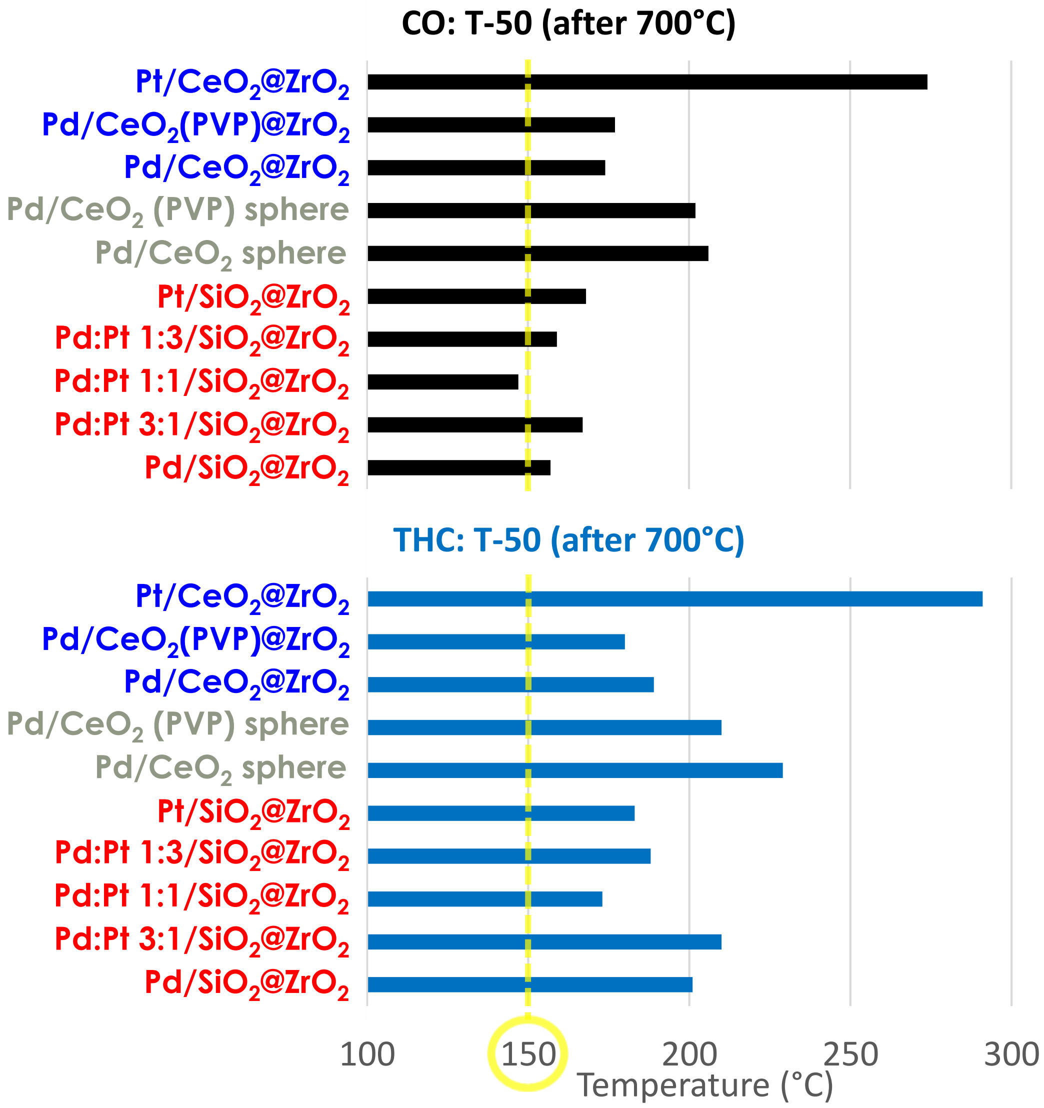
$CeO_2@ZrO_2$



CeO_2 sphere



$SiO_2@ZrO_2$



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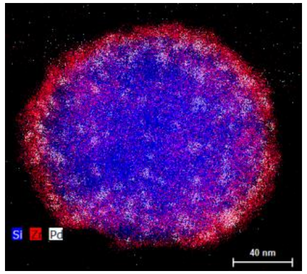
NO:	100 ppm
H_2:	400 ppm
H_2O:	6 %
CO_2:	6 %
O_2:	12 %
Balance N_2	

T-50s used here as an initial evaluation point. High conversion was delayed due to the use of fine powders that cause diffusion limitations

Further aging novel catalysts shows notable improvements; comparing to commercially-available PGM catalysts quantifies progress

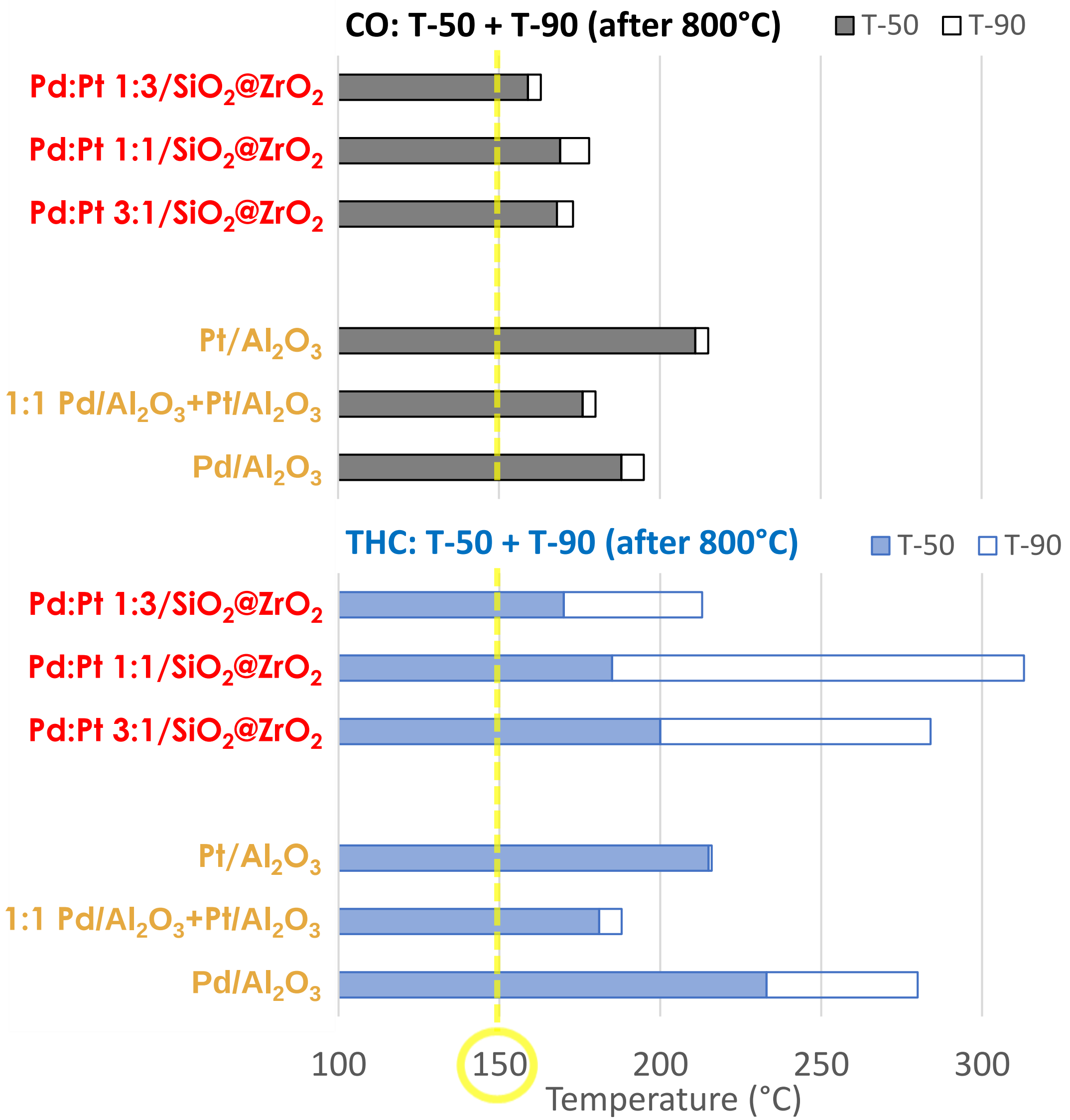
- Pt:Pd supported on $SiO_2@ZrO_2$ continue to show good activity
- Aging at 800°C shows minimal loss in CO activity and THC T-50
  - T-90 for THC is notably delayed
  - possible improvements with washcoating
- Purchased baseline materials from Sigma-Aldrich to provide commercial standard for comparison
  - 1% Pd/alumina and 1% Pt/alumina catalysts
  - Evaluated individually and in a physical mixture (Pd + Pt)



Pd or Pt on $SiO_2@ZrO_2$

SIGMA-ALDRICH

1%wt Pd or Pt on Al_2O_3 (Pd+Pt is a physical mixture)



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NO:	100 ppm
H_2:	400 ppm
H_2O:	6 %
CO_2:	6 %
O_2:	12 %
Balance N_2	

T-50 and T-90s used here as the powders were sieved to 250-500 microns to minimize diffusion limitations at high conversions

Technical Accomplishments

- Passive NOx Adsorbers
  - Understanding deactivation
  - Investigating new formulations
- Oxidation Catalysts
  - Core-shell PGM support
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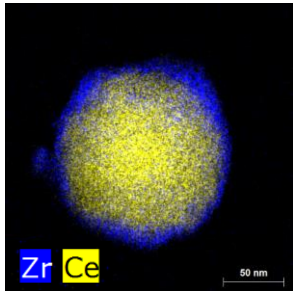
- Stoichiometric TWCs
  - Applying novel catalysts as TWCs

PGM supported on CeO_2@ZrO_2 shows promising results for TWCs

- Same family of catalysts evaluated under LTC-D conditions
  - Pt/CeO_2@ZrO_2
  - Pd/CeO_2@ZrO_2
  - Pd/CeO_2(PVP)@ZrO_2
- Evaluated after hydrothermally aging at 800°C
- All show similar behavior for CO, THC, and NOx
- Compared to Sigma-Aldrich samples, the **Pt/CeO_2@ZrO_2** formulation shows remarkable improvement

T-50s used here since fine powders of novel catalysts were used in an initial evaluation



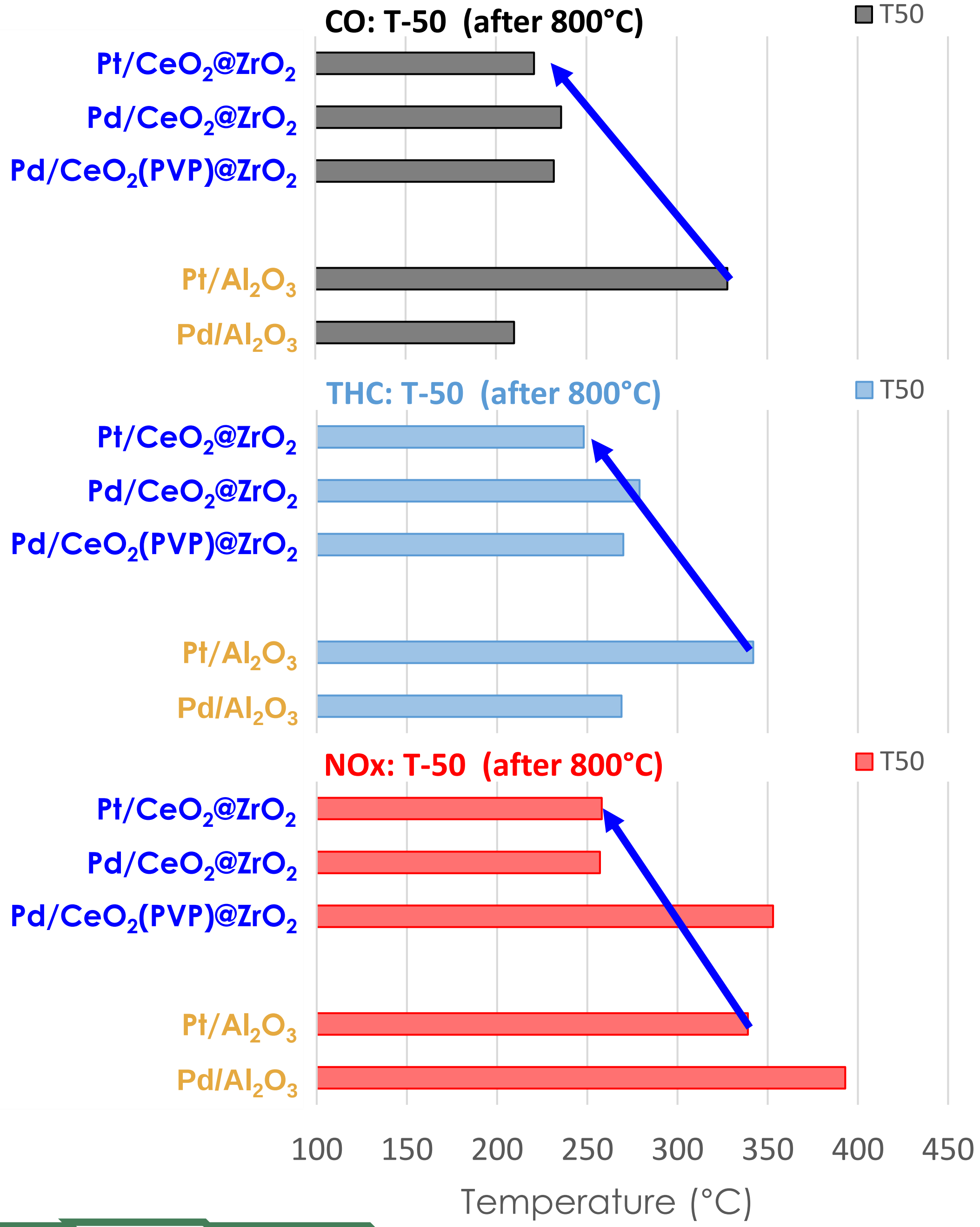
CeO_2@ZrO_2

SIGMA-ALDRICH

Pd or Pt on Al_2O_3

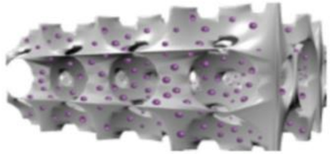
S-GDI: Stoich. Gasoline Direct Injection

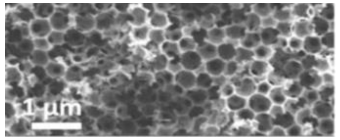
Total HC_1:	3000 ppm
C_2H_4:	1050 ppm
C_3H_6:	1500 ppm
C_3H_8:	450 ppm
i-C_8H_{18}:	0 ppm
CO:	5000 ppm
NO:	1000 ppm
H_2:	1670 ppm
H_2O:	13 %
CO_2:	13 %
O_2:	0.74 %
Balance N_2	



Evaluated interesting highly porous and stable support from Metalmark as TWC

- Collaboration initiated with Harvard's Wyss Institute
  - Approached us with a subset of data that looked promising
  - We then agreed to evaluate samples under CDC, LTC-D, and S-GDI oxidations protocols
  - 0.57% Pd or 1.0% Pt on Al_2O_3
- Results shown are after aging for 50h at 800°C
  - Results for S-GDI look promising and show improvement over the Sigma Aldrich Pd/Al_2O_3
  - Results for LTC-D and CDC are also comparable





**Metalmark 0.57% Pd or 1%Pt on Al_2O_3*

SIGMA-ALDRICH

1% Pd or Pt on Al_2O_3

S-GDI: Stoich. Gasoline Direct Injection

Total HC_1:	3000 ppm
C_2H_4:	1050 ppm
C_3H_6:	1500 ppm
C_3H_8:	450 ppm
$i\text{-}C_8H_{18}$:	0 ppm
CO:	5000 ppm
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H_2:	1670 ppm
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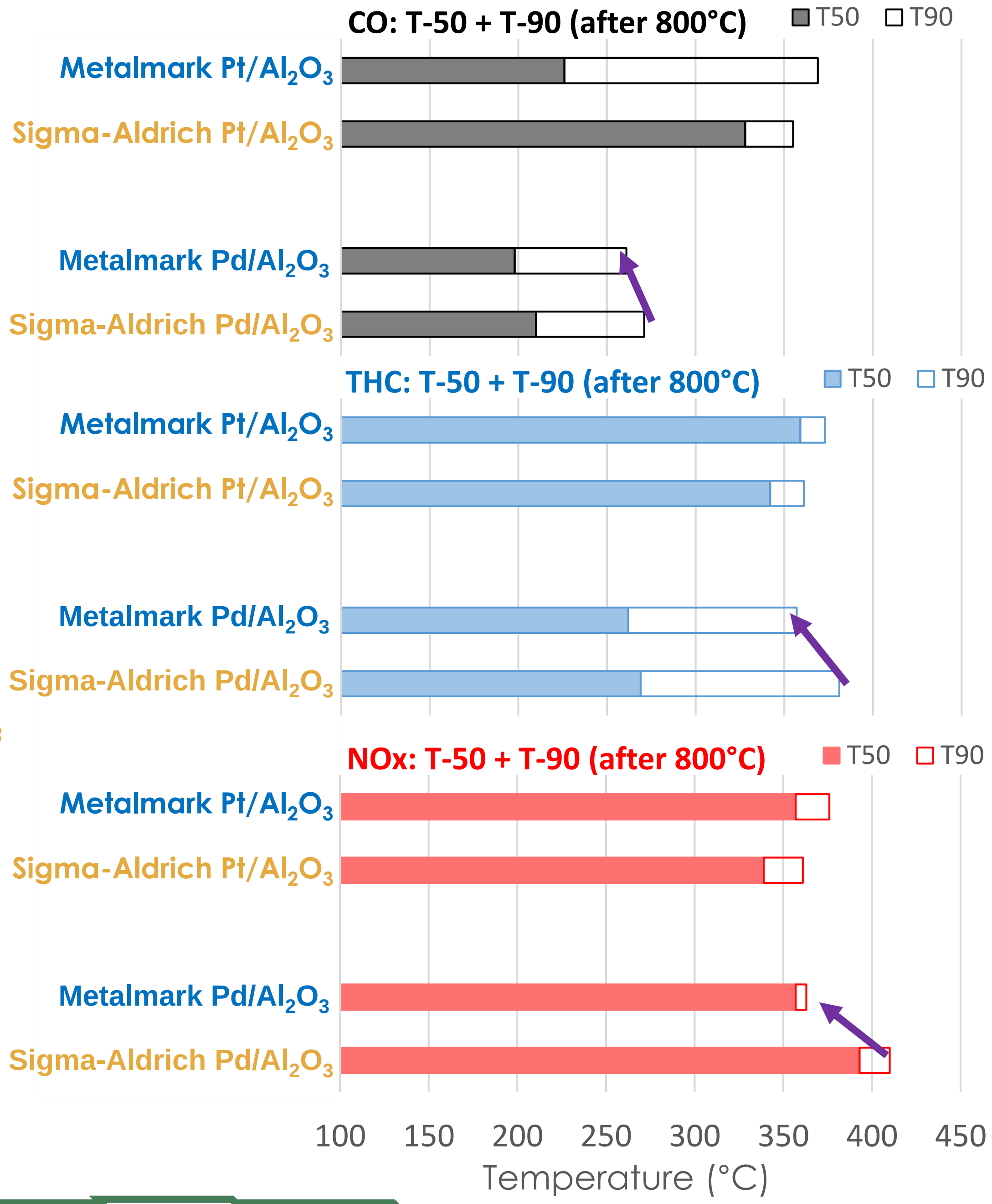


* - Images from upcoming publication: T. Shirman et al. "Raspberry colloid-templated approach for the synthesis of oxidation palladium-based catalysts with enhanced hydrothermal stability and low-temperature activity," Accepted to Catalysis Today (2020).

Remaining Challenges

Future Directions

- **Trap Materials**

PNA: NOx uptake needs to be stabilized

Evaluate new formulations with continued focus on durability; investigate methods of limiting CO exposure or drawing it away from the Pd

HCT: Increased storage capacity of lighter HCs necessary

Investigate other zeolites and formulations listed in PNA section, including fully non-PGM formulations; combine HCT and PNAs with oxidation catalyst

- **Oxidation Catalysts**

Need improved oxidation of HCs after aging

Continue to evaluate supports that are already made with emphasis on ceria-based supports

Move to minimize diffusion constraints in catalysts such that T-50 is similar to T-90; including initiating washcoating procedures

Expand collaboration with Harvard University/Metalmark Innovations with more supports and bi-metallic formulations

- **Stoichiometric TWCs**

Enhanced low temperature reactivity with minimum PGM

Investigate formulations with lower levels of PGM; evaluate oxygen storage capacity/kinetics; install valves to allow evaluation while dithering

Any proposed future work is subject to change based on funding levels

Summary

- **Relevance:** Develop new emission control technologies to enable fuel-efficient engines with low exhaust temperatures (<150°C) to meet emission regulations
- **Approach:** employ low temperature protocols to evaluate novel catalysts and systems
- **Collaborations:** Wide-ranging collaboration with industry, academia, other DOE projects, & national labs maximizes breadth of study, guides research from other funding sources
- **Technical Accomplishments:**
  - *Trap Materials*: Identified CO as primary deactivation agent in PNAs; Showed CO and unsaturated HCs enhance NO uptake in PNAs; Illustrated HCs/H_2 do not cause deactivation; Synthesized novel PNA materials
  - *Oxidation Catalysts*: Evaluated a wide range of PGM/core@shell oxidation catalyst/support combinations with some showing progress to 150°C challenge; Established baseline commercial material to compare progress
  - *Stoichiometric TWCs*: Using novel CeO_2@ZrO_2 formulations showed improved activity compared to the baseline commercial material when using Pt; Illustrated improvements with Pd catalyst from collaborative partner Metalmark Innovations
- **Future Work:**
  - *Trap Materials:* Evaluate new formulations with continued focus on durability while limiting CO exposure to or drawing it away from Pd; Investigate other zeolites, including fully non-PGM formulations; combine HCT+PNA
  - *Oxidation Catalysts*: Continue full-scale evaluation with emphasis on ceria-based supports; Move to minimize diffusion constraints in catalysts; Initiate washcoating procedures; Expand collaboration with Metalmark
  - *Stoichiometric TWCs*: Investigate formulations with lower levels of PGM; Evaluate oxygen storage capacity/kinetics; Install valves to allow evaluation while dithering

Any proposed future work is subject to change based on funding levels

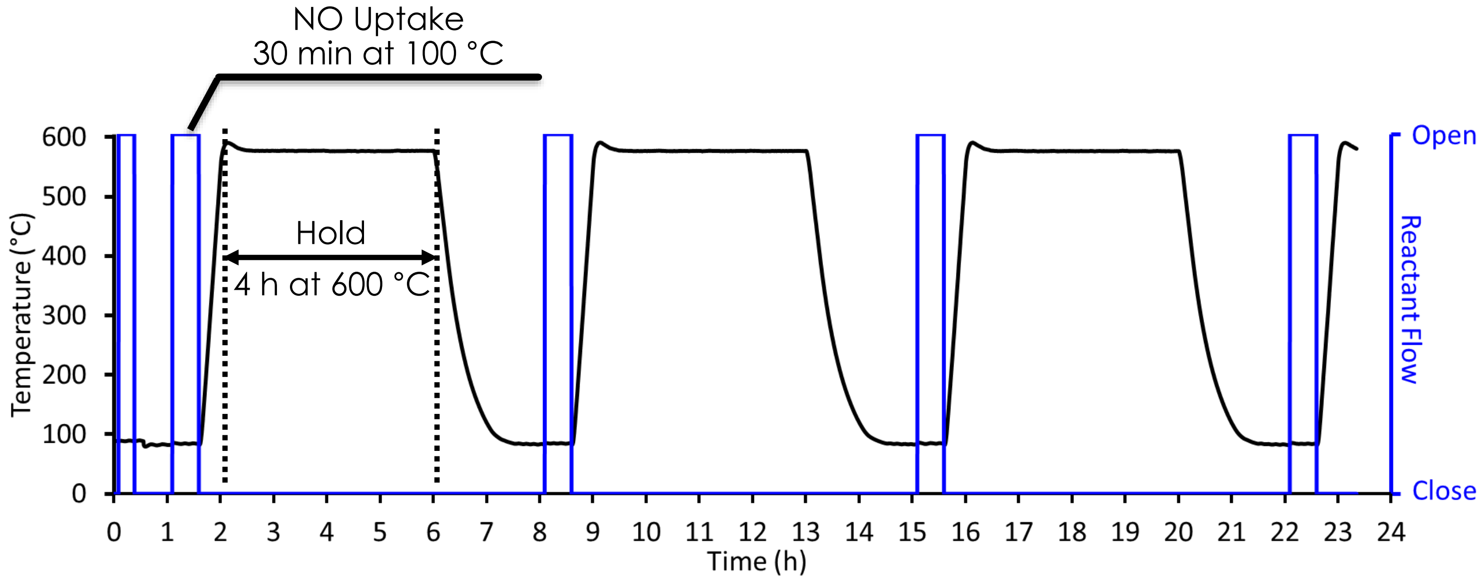
Technical Backup Slides

PNA and HCT evaluation protocol

- Repeated measurements to evaluate stability
- Using gases for oxidation protocol since this will eventually be used for a multi-component evaluation with oxidation catalysts

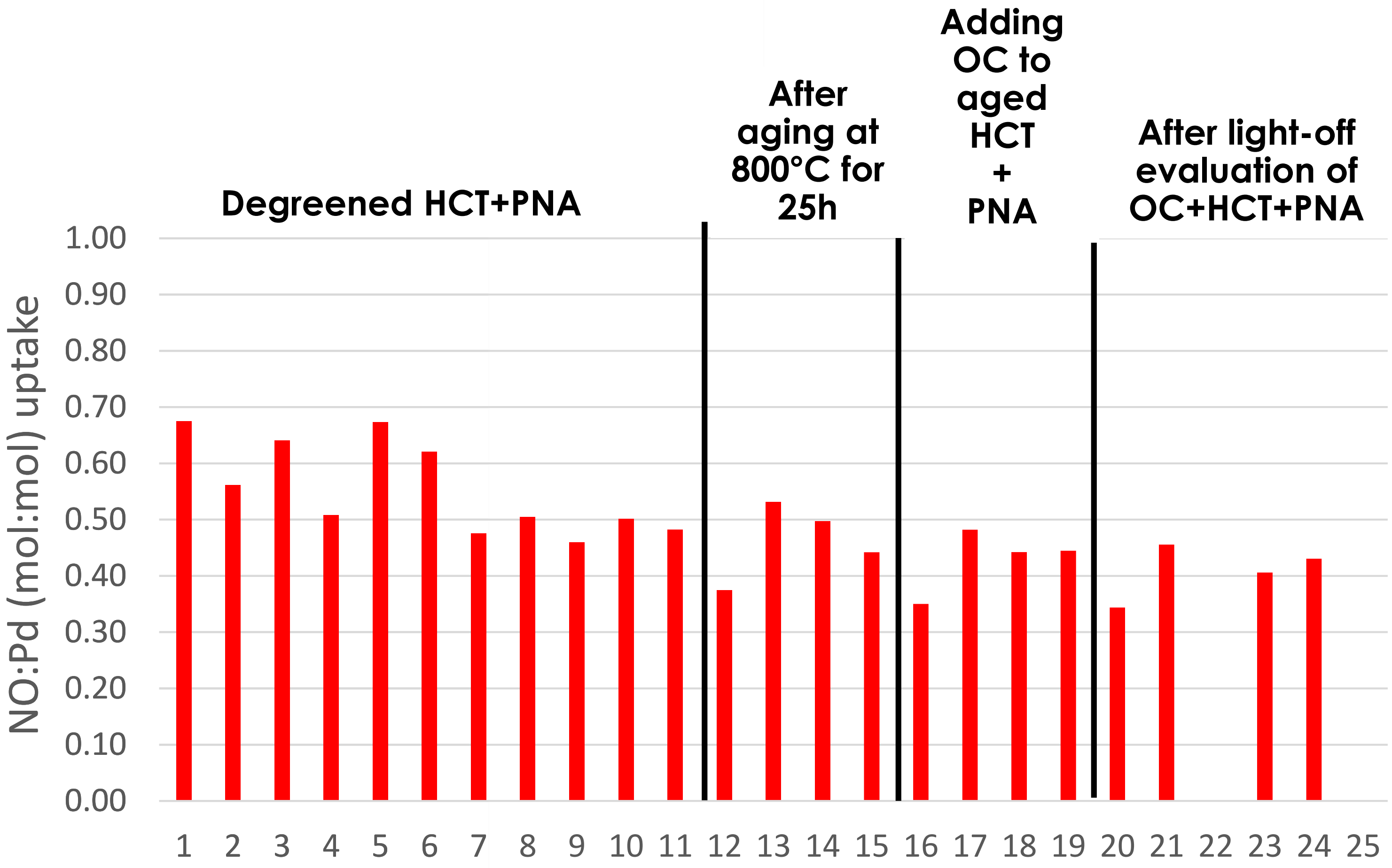
- Pd/SSZ-13 | Ion-exchange
- Air Calcination | 500 °C, 5 h

LTC-D: Low Temp. Combustion Diesel	
Total HC_1:	3000 ppm
C_2H_4:	500 ppm
C_3H_6:	300 ppm
C_3H_8:	100 ppm
$C_{10}H_{26}$:	2100 ppm
CO:	2000 ppm
NO:	100 ppm
H_2O:	6 %
CO_2:	6 %
O_2:	12 %
Balance Ar	



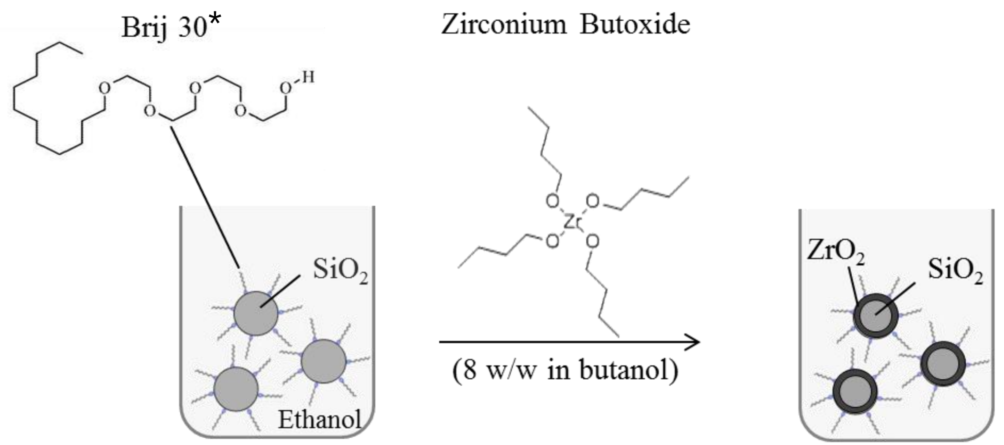
PNA combined system repeated evaluations

- Last year in combined system there were suggestions that the deactivation was slowed
- However, after repeated evaluations deactivation is still observed
- Possible slowing due to CO interacting with OC and HCT



New approach: Cover all of the SiO_2 surface with Zr

Synthesis of SiO_2@ZrO_2 core@shell Oxide Support

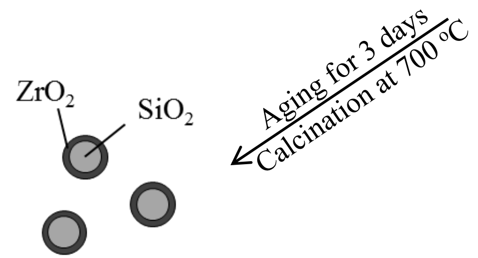


Synthesis of silica spheres

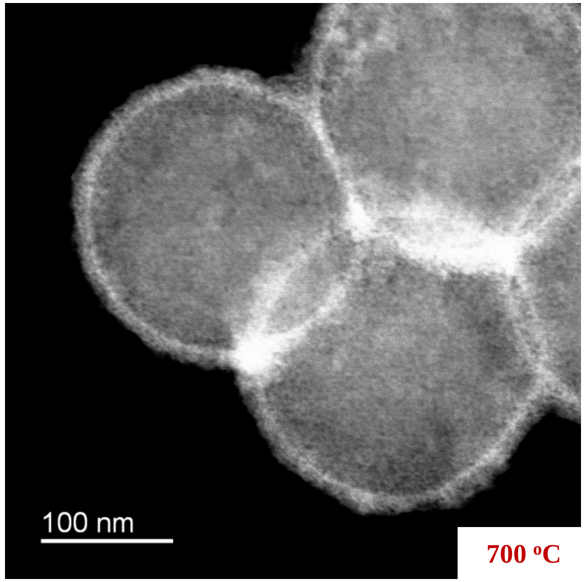
Silica core and amorphous shell with zirconium hydroxide

*(Brij 30): Polyoxyethylene(4) lauryl ether

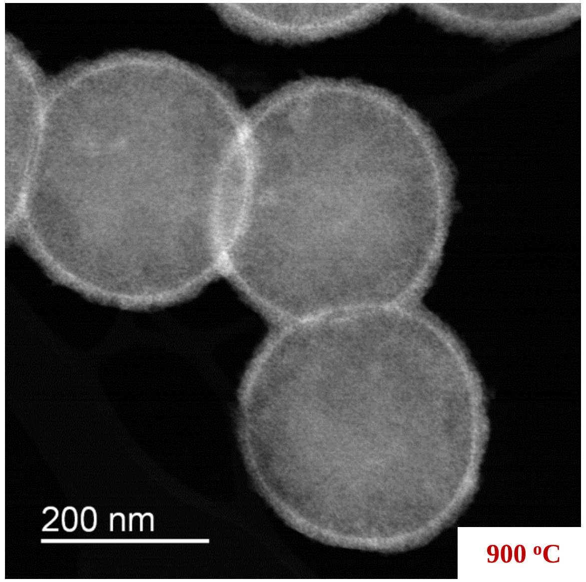
Material	Surface Area (m^2/g)
ZrO_2	97
ZrO_2-SiO_2	153
SiO_2@ZrO_2	**210**



Silica core and zirconium oxide shell after calcination at 700 °C



700 °C

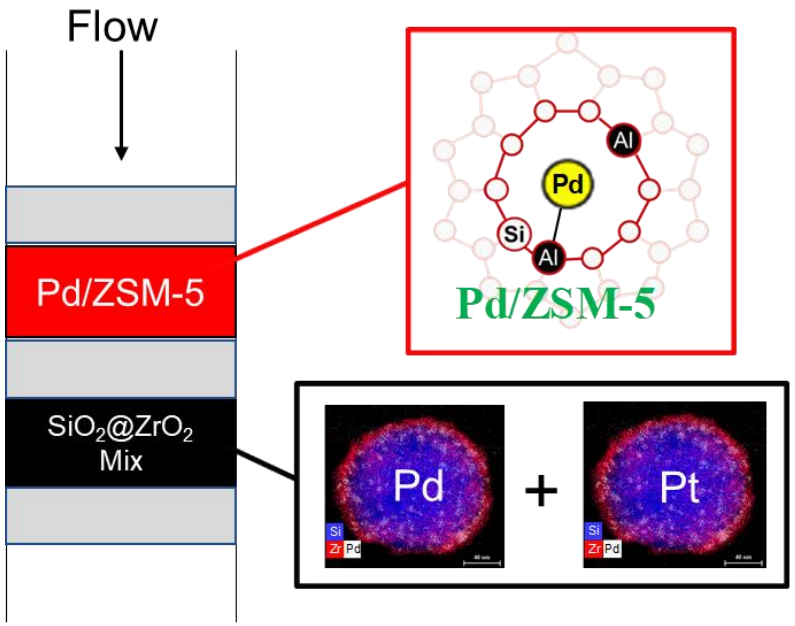


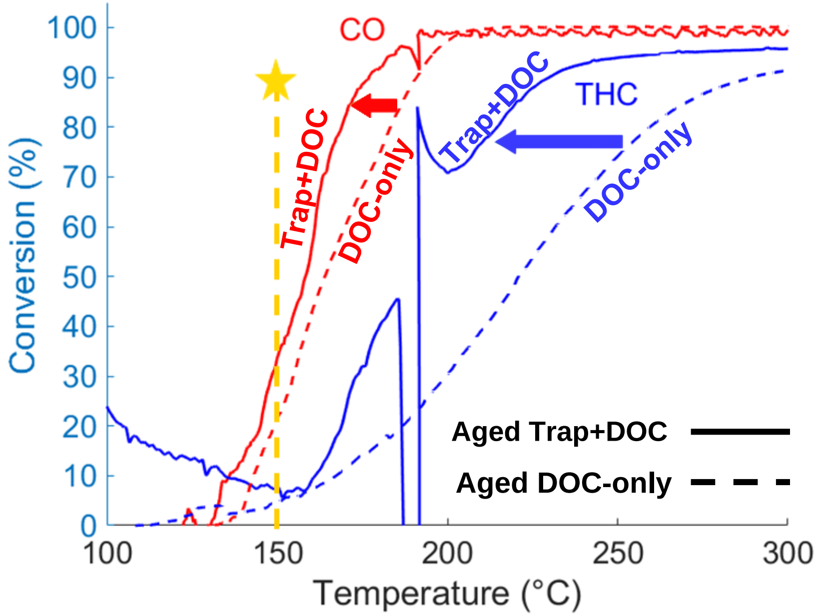
900 °C

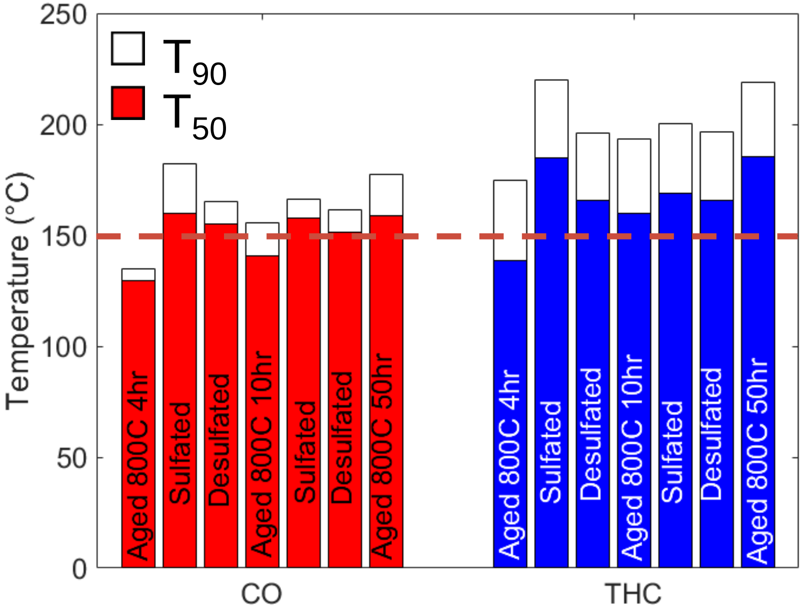
- **SiO_2** is located in the **core** and **ZrO_2** in the **shell**
- The ZrO_2 **shell** seems to be **porous**
- Growth of SiO_2@ZrO_2 spheres. Shell is maintained. Diameter at: **900 °C: ~250 nm**

Support: P.M. Arnal, C. Weidenthaler, F. Schüth, Chem. Mater. 18 (2006) 2733-2739.

Trap materials + oxidation catalysts significantly improve overall system functionality after aging







Protocol aging: reaction conditions at 800°C for 50h, 5 ppm SO_2 @ 300ºC 5 h
Desulfation under cycling lean-rich conditions for 30 min at 500ºC, 30s per condition

- Although Pd/ZSM-5 trap is heavily degraded, it still improves reactivity of system considerably in dual-bed configuration

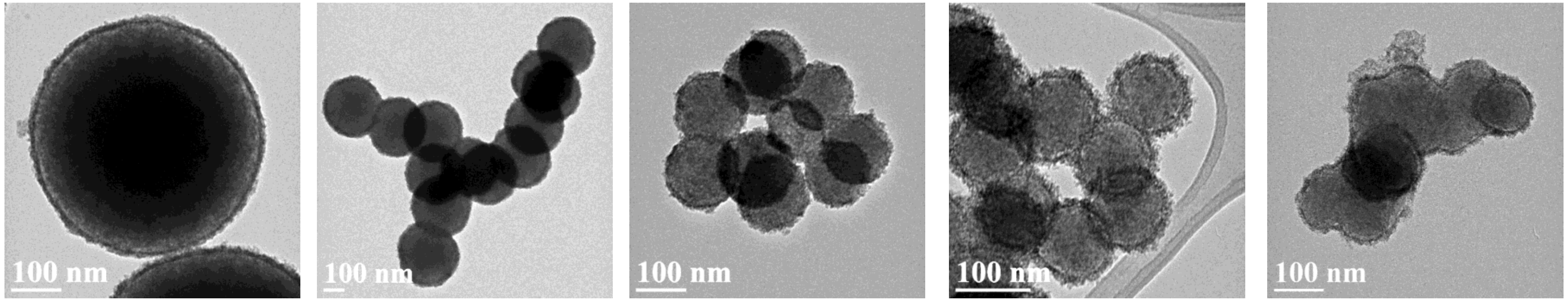
Conditions during 2ºC ramp

total HC_1:	*3000 ppm*
C_2H_4:	*500 ppm*
C_3H_6:	*300 ppm*
C_3H_8:	*100 ppm*
$C_{10}H_{22}$:	*2100 ppm*
CO:	*2000 ppm*
NO:	*100 ppm*

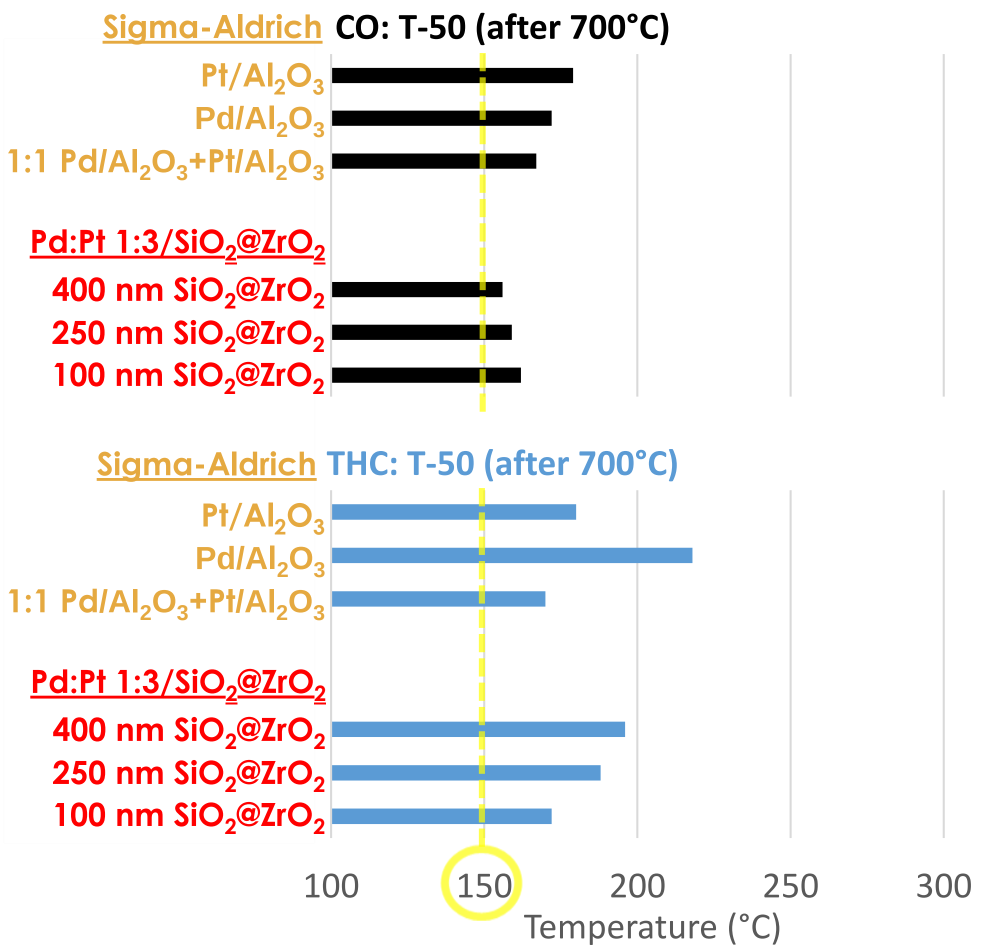
Also H_2, O_2, H_2O and CO_2

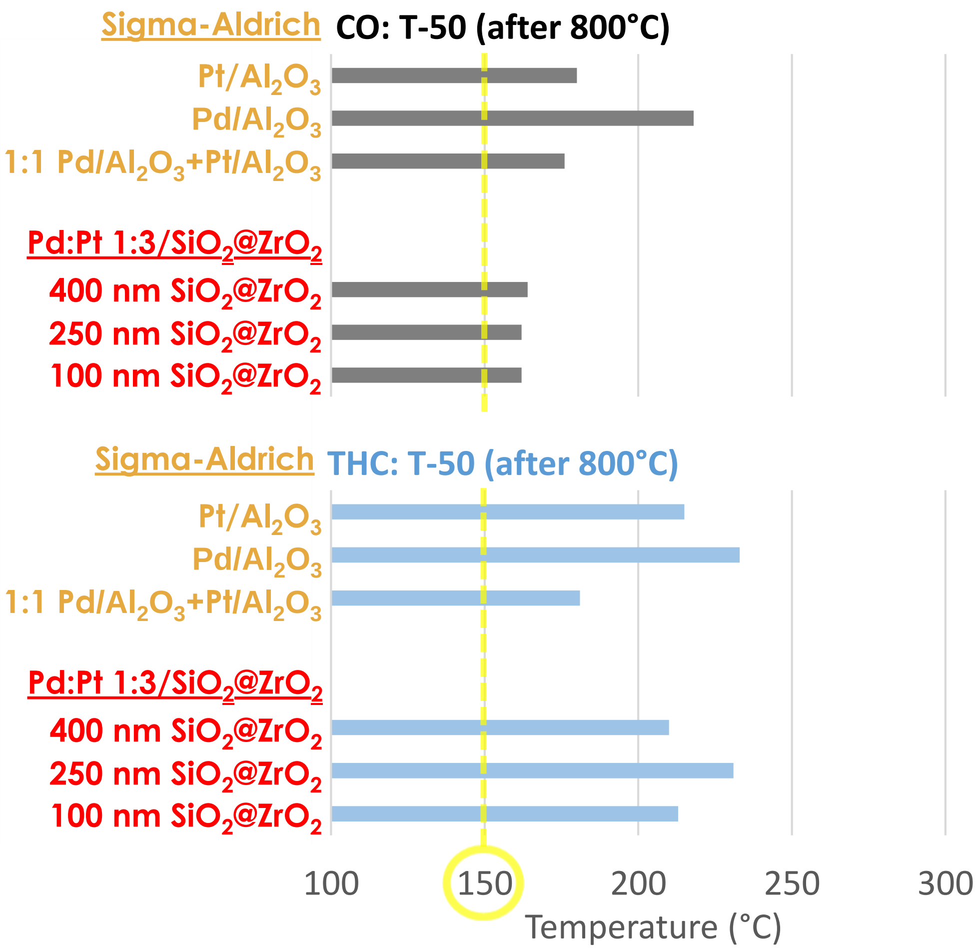
SiO_2@ZrO_2 core@shell size effects in LTC-D

- Synthesized range of core-shell support sizes 100-450 nm
- Evaluated in LTC-D oxidation protocol
  - Used fine powders
- Each compares favorably to **Sigma Aldrich**, but no trend apparent



~490 nm | ~290 nm | ~150-200 nm | ~120 nm | <100 nm





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H_2:	400 ppm
H_2O:	6 %
CO_2:	6 %
O_2:	12 %
Balance N_2	